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### THE DEVELOPMENT

—OF THE—

# PERIODIC LAW

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-BY----

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90405

EASTON, PA.: CHEMICAL PUBLISHING CO. 1896.

9D 467 V44

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#### PREFATORY SKETCH.

This work is intended as a study of the development of the natural law underlying the relations of the elements and their properties to one another. It is to be used for purposes of reference and of study and not as a mere history of the subject. The errors and repetitions of the writers upon this subject in the past few years have abundantly proved the necessity for some such gathering and systematizing of the work of former years. It is, in the main, an out-of-the-way sort of literature and the difficulty of gathering it increases with the lapse of time. The growing interest in this natural law speaks well for the progress of the science in the future. More and more it is becoming recognized as the basis of the science, and the hope of the solution of some of the greatest problems which the chemist has to face seems to lie in it. The reproach that chemistry is not, in the fullest sense, a science will continue just so long as chemists content themselves with raking together the straws of facts, gleaners many of them in a harvested field, and neglect the "weightier matters of the law." The gathering of facts is good, gleaning is good, but contentment with such gains means stagnation.

The task has been undertaken in the hope of arousing interest in this matter and of aiding in the further development of the still incomplete system. No excuses are offered for the imperfections of the work. It could not be other than imperfect. The task has been most

difficult, and the limitations of the writer have been felt at every turn. It has been done as conscientiously and impartially as was possible. Doubtless many authors will find cause for disagreement with the treatment accorded their work. The reception of Newland's Law of Octaves, by the London Chemical Society, and many other instances of mistaken judgment, show how difficult it is to weigh these matters fairly and wisely.

Since there may be some who do not care to make a study of the whole subject, but would like to take a connected glance over it, this preface will be turned into an historical sketch of the law's development, omitting the mass of details to be found in the remainder of the work. Such a sketch may prove useful to others also.

Before the atomic theory was formulated, numerical relations were proposed by Richter, the founder of Stoichiometry, between the equivalents obtained by him for the various bases and acids. This mathematical work of his served but little purpose beyond bringing the whole subject of his equivalents into some disrepute. Only a few years passed after the publication of the first tables of atomic weights before their inter-relation became a subject of speculation and research. In 1815 we have Prout pointing out the strange fact of their close approximation to whole numbers and boldly rounding them off into such. If they were integral multiples of hydrogen, he reasoned, then this might be the primal matter and all elements made up of it. The "Multiplen-fieber" quickly took possession of the chemical world, even of conservative, level-headed workers such as Berzelius. Enthusiastic support was given if by the English chemists especially and, when Berzelius afterwards became its great antagonist, Thomson and others busied themselves in its defense. The newly organized British Association devoted its freshenergies to an examination into the condition of the various sciences and. among other inquiries, set on foot one as to the grounds for believing in what was then called and has been often so called since. Prout's Law. The result of this inquiry was adverse to the "law" and it would have been dropped, in all probability, had it not been taken up by Marignac, Dumas, and the French chemists, with certain modifications rendered necessary by the more perfect knowledge of the atomic weights. Probably no other hypothesis in chemistry has been so fruitful of excellent research as this much discussed hypothesis of Pront.

Meanwhile, a different style of numerical regularity had been brought to the notice of chemists. In 1817, Döbereiner first noticed a strange grouping of analogous elements into threes, or triads as they soon came to be called. The intermediate member of such a triad showed itself to be a mean of the other two in atomic weight and other properties. Döbereiner was at first inclined to think that this could only mean that the intermediate element was a compound of the other two. His effort at arranging all of the elements into triads failed. Still he did the science great service in arranging the elements according to their atomic weights. It was a great lightening

of the task of both teacher and student and hence found ready entrance into the text-books, especially that of Leopold Gmelin, the most influential chemical writer of the times.

For twenty years, little was added to the work of Döbereiner. Little could be done with the imperfect and incomplete tables of the atomic weights then in use. Dumas and others had been busy in the revision of many of these constants and his mind was thus especially drawn to their numerical regularities. meeting of the British Association at Ipswich in 1851, he delivered a lecture, embodying his ideas as to the possible composite nature of the elements and giving instances of remarkable relations existing between their atomic weights. This attracted the earnest attention of chemists everywhere. Reports of the lecture were published in the scientific journals of various countries. Hopes were aroused in very conservative chemists that the dissociation of the so-called simple bodies, which for half a century had been looked upon as made up of undecomposable atoms, was a possible achievement of the near future. It would transport one to dreamland at once to think of what could be accomplished if once the secret of the composition and dissociation of these elements was in the grasp of the chemist.

A diligent company of thinkers, workers, and also visionary speculators sprang up. The most prominent characteristic of the work of the period was the digging out of arithmetical regularities and relations between the numbers representing the atomic weights. Strict accord

was not demanded. Approximations ruled the day, and the reputed laws discovered were justified by the appeal to the laws of probabilities. It was easy to calculate out, as De Morgan did, that the probabilities were greatly against such and such a number of approximate coincidences occurring by accident. But little attention was paid to the other properties of the elements and their connection with the atomic weights, though in many cases the isomorphism of salts was made use of as determining the analogies of the elements. The triads of Döbereiner were completed and pushed far beyond the speculations of their author. There were efforts at combining them into enneades and securing a net-work of elements. Algebraic formulas were sought for, by means of which it would be possible to calculate the various atomic weights. The regularities observed among the homologous series of organic chemistry were appealed to in the hope of solving the mystery of the singular regularities which undoubtedly existed. For one must not think of these workers, some of them chemists of great reputation, as being entirely misled. Of course a great variety of relations are always to be observed between sixty odd numbers taken out of a little more than two hundred, especially if one is not over particular in insisting upon exact coincidences. There are interesting numerical relations actually existing between these atomic weights, first noticed at the time of which we are speaking and still without any plausible explanation.

In this period will be found the triads of Kremers, Lennsen, and Odling; the homologous series of Cooke,

Dumas, and Mercer; the double parallelism of Dumas; and the atomic weight differences of Dumas, Pettenkofer, and Lea. There was also the first attempt at arranging the atomic weights in an ascending series according to their increasing magnitude. This was by Gladstone, and is looked upon now as one of the fundamental features of the periodic system. No results were obtained at that time by this arrangement because the atomic weights used were very faulty, a large number of them being placed at about half the values at present assigned to them. It is not surprising that the hopes first aroused as to any valuable results flowing from these speculations were disappointed, and with the disappointment seems to have come a general discrediting in the public mind of all such work. Chemists of note apparently dropped the subject, some wrote anonymously, and really meritorious work was received either with silence or ridicule. It is only just to state that, so far as any hopes of the immediate solution of the problem of the constitution of the elements was concerned. Dumas had been careful to discourage them.

The first gleam of hope of an improved condition of affairs came through the introduction of more accurate atomic weights by Cannizzaro. Williamson aided in the introduction of these in England. With these it became possible to see relations which had been obscured before. An arrangement of the atomic weights in an ascending series now revealed something of that periodicity which has since proved such a valuable thought to inorganic chemistry. The first to arrange

them in this way was the French engineer and mineralogist de Chancourtois. His Telluric Screw contained much of the essential truth that lies in the periodic law. Along with it, there was of course, error and confusion with useless detail. It is easy to see in this, now, the germs of Mendeléeff's later discovery. Chemists of the day, however, were not in a position to sift out the false, and hence the whole scheme received little or no attention, and remained hidden in the publications of the French Academy of Sciences, to be unearthed a quarter of a century afterwards, by two French chemists.

Following this came the presentation of the Law of Octaves by Newlands, before the London Chemical Society. Here the ascending series and the periodicity were still more clearly brought out. There was much less of the false and less of confusing detail. A thought, which was largely lacking in the work of the previous decade, begins to appear here. That is, the dependence of the properties upon the atomic weights. The same is true of the system of de Chancourtois. And yet, possibly because of the fanciful name given by Newlands implying a unity of his system with that of music, the Society accorded him chiefly ridicule for his effort, and it took them twenty years, or more, to find out their mistake.

Almost at the same time with the announcement of Newland's law, Meyer published his first work upon the Modern Theories of Chemistry, a work destined to a life of many editions and much fame and usefulness, and in this he gave the first of his tables of the atomic weights, the precursor of his periodic system. This certainly failed to give even as clear an idea of periodicity as the table of Newlands, and required a great deal of evolution before it could bear much resemblance to the completed table. Almost at the same time we have the announcement by Hinrichs that the properties of the elements are functions of their atomic weights and that the unity of matter was as real as the unity of force. These were the precursors of the periodic law. They failed of recognition for many reasons, though two chief ones can be assigned; first the public was wearied with, and distrustful of, such speculations; secondly, they were incomplete, and in some respects, overweighted with error.

When Mendeléeff, in 1869, announced the new "Natural System," as he at first called it, one keensighted observer reported it as something that would prove interesting and probably useful, but no great stir was created, such as was noticed at the delivery of Dumas' address. In a very short time appeared the almost identical system of Meyer, evolved from his earlier tables but modified somewhat by his study of the table of Mendeléeff. To these two men the Royal Society of England gave the highest medal in its gift as the discoverers of the greatest law of modern chemistry. To one, or both, the credit undoubtedly belongs. They were both in ignorance of the previous work of de Chancourtois and of Newlands and they presented the system in such a shape that it was useful for many purposes and could be put to the test as to its truth and value. Still the system aroused little comment and was threatened with the same fate of dust and oblivion which had befallen the systems of earlier writers. After several years of neglect, even on the part of its authors, attention was drawn to the system once more by the fortunate fulfilment of certain bold predictions made by Mendeléeff in his table. The discovery of scandium and gallium and their fitting into the predicted places, with atomic weights and other properties coinciding with those predicted for them, gave a new impetus to the study of these tables and their use in the class-room. Many results have sprung from this. Increased diligence has been observed in the revision of faulty atomic weights; new interest has been shown in the advancement of the knowledge of inorganic chemistry; the inter-relation of the elements has become so clear that one is forced to the conclusion that they are composite in nature, even though the nature of the relationship is unknown, and no immediate hope is held out of solving the problem. The question of the variability of the atomic weights, suggested by Marignac and discussed by Cooke, Schützenberger, Boutlerow, and others, seems untenable in the light of the periodic system and so too with the hypothesis of Prout, at least in its original form, presenting hydrogen as the original element. This hypothesis had been laid to rest by the wonderfully accurate atomic weight determinations of Stas, but was revived again by its old defender, Dumas, to receive a fitful sort of discussion for a few years and be accorded a tentative, halfway support on the part of a few distinguished chemists.

Its original features have now been lost and it has become identified with the theory of the unity of matter and the idea of the composite nature of the elements. In this form it is simply one of the natural deductions from the periodic law, although Mendeléeff would discourage all such dreams and denies that they are to be justly deduced from his law.

Those who read the later pages of this work will see how far from complete this periodic system is. Its imperfections are many, but they are outweighed by its virtues and the truths which it so well presents. That there can be a better presentation of them is most likely; that it is just beginning to reveal all of the truths which it is capable of revealing is also true. It demands of the chemist careful study. The close of this century calls loudly for another Lavoisier, who shall interpret the facts won by such hard toil and place the science on the right track for another century of brilliant progress and discovery.

## The Development of the Periodic Law.

#### CHAPTER I.

I. Prout's Hypothesis and Doebereiner's Triads.— The study of the development of the natural arrangement of the elements, the gradual crystallization of the ideas concerning the laws underlying the numerical relations of the atomic weights into definite form, is one of great importance to the science of chemistry. Like other secrets wrested from nature, this has been no sudden discovery, but is the result of the thought and labor of many years. In speaking of this development, it should be clearly understood that it is not to be considered complete, nor that the process of evolution is finished, nor that the natural system stands before us to-day in its full and perfect form. Much progress has been made, but there is growth in these ideas, and hence it is incumbent upon chemists to make a more thorough study of what has been done and so prepare themselves to aid in further progress. The natural system has already become the central fact of the science. It has dispelled many errors, it has inspired much true work, it points to the solution of some of the greatest problems which we have to face.

The study of this development will be pursued chronologically, and though there is at times much temptation to follow up some special idea, as that of the triads, and bring together in one place all work referring to it, there will be only a few brief excursions of the kind.

It would seem that there is some great fascination connected with the search after numerical relations among the atomic weights. From the very first the possible discovery of some mysterious law or the dream of the Unity of Matter has lured on investigators and dreamers. Prout was the first one to point out a numerical relation on which he based his famous hypothesis. To show the material with which he worked, it will be necessary to discuss the early tables of atomic weights.

2. The Unity of Matter.—The question as to the nature of matter is one of the great world-problems constantly attracting and eluding man's research. For centuries the mind of man has dwelt on this problem without success, beyond certain plausible, yet unsatisfactory speculations, and still he is not willing to give up the problem as one beyond his powers of solution. The trend of thought has been toward simplification, a reduction of matter to its simple components and a unification in one primal component if possible, thus bringing matter into line with the great unities of the universe.

The Greek dream of atoms has found justification and fulfilment in the research and learning of this century. The old-world idea of unity or of a primal element has its followers at the present day who believe we are verging upon such discoveries as will confirm that also, going deeper into the nature of matter than the material, ponderable atoms. This is a close approach to the Pytha-

gorean idea of the infinite divisibility of matter yet should not be confused with it as some have done.

Dalton's revival of the atomic hypothesis at the beginning of this century gave additional meaning and importance to Lavoisier's definition of the elements, and from that time we have these two ideas, element and atoms, forming the very basis of the science of chemistry. These ideas have not been introduced without some opposition, some confusion and lack of clearness of definition, but they have successfully fought their way and become more clearly defined.

As the century draws to its close the thought is gaining ground that these elements are not really simple bodies, but that their material atoms are composed of other forms of matter, and the hope rises that through these the way may be traced to the old elusive primal matter.

3. Definition of Element.—With increasing knowledge the exact definition of an element has become more and more difficult. The observation of the phenomena of allotropism overthrew the older definitions. Perhaps the one given by Patterson Muir (218, p. 6)<sup>1</sup> is the most satisfactory. "The notion of the elements that has been attained after long continued labor is that of certain distinct kinds of matter, each of which has properties that distinguish it from every other kind of matter, no one of which has been separated into portions unlike one another and unlike the original substance, and

<sup>&</sup>lt;sup>1</sup> The figures in parentheses refer to Index to Literature at the end of the volume.

which combine together to produce new kinds of matter that are called compounds." Again he speaks of the term being used more and more to designate certain groups or assemblages of associated properties (218, p. 31). It is one of the objects of these pages to sum up all that has been said about the numerical inter-relations of the atoms of these elements, and show just how much ground the speculations as to a primal matter have for their basis. The literature on the subject is difficult of access; there much is ignorance as to this literature, and a knowledge of it may save chemists from much repetition and from useless vagaries.

4. The Atomic Weights of Dalton.—The concluding paragraph of a paper read by Dr. John Dalton before the Literary and Philosophical Society of Manchester, October 21, 1803, upon "The Absorption of Gases by Water and other Liquids" is as follows:

"The greatest difficulty attending the mechanical hypothesis, arises from different gases observing different laws. Why does water not admit its bulk of every gasalike? This question I have duly considered, and though I am not yet able to satisfy myself completely, I am nearly persuaded that the circumstance depends upon the weight and number of the ultimate particles of the several gases, those whose particles are lightest and single being least absorbable, and the others more, accordingly as they increase in weight and complexity. (Subsequent experience renders this conjecture less probable). An inquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new: I

have lately been prosecuting this inquiry with remarkable success. The principle cannot be entered upon in this paper: but I shall just subjoin the results, as far as they appear to be ascertained by my experiments."

DALTON'S "TABLE OF THE RELATIVE WEIGHTS OF THE ULTIMATE PARTICLES OF GASEOUS AND OTHER BODIES."

| Hydrogen                                  | •    |
|---|------|
| niyarogen                                 | 1.0  |
| Azot ·····                                | 4.2  |
| Carbone                                   | 4.3  |
| Ammonia                                   | 5.2  |
| Oxygen ·····                              | 5.5  |
| Water                                     | 6.5  |
| Phosphorus                                | 7.2  |
| Phosphoretted hydrogen                    | 8.2  |
| Nitrous gas                               | 9.3  |
| Ether                                     | 9.6  |
| Gaseous oxide of carbone                  | 9.8  |
| Nitrous oxide                             | 13.7 |
| Sulphur                                   | 14.4 |
| 271. 1 11                                 | 15.2 |
| 0.1.1 1.1                                 | 15.4 |
|   | 15.3 |
| 44 4 4                                    | 15.1 |
| 0.1.1.                                    | 19.9 |
| A 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1   | 25.4 |
| Carburretted hydrogen from stagnant water | 6.3  |
| Olefiant gas                              | 5.3  |

This was the first attempt at a table of the atomic weights. Elements and compounds are considered together and the numbers given are, of course, very faulty. Richter's earlier table of the equivalents of various substances can scarcely be considered in the same light as

Dalton's. These were mainly acids and bases and it was purely a stoichiometrical table.

In the year 1808 appeared Dalton's New System of Chemical Philosophy. In this he gives a table of the atomic weights of thirty-seven substances, again taking hydrogen as the unit and standard.

5. Remarks of Roscoe on Dalton's First Table of Atomic Weights.—Doubtless many chemists have wondered how these first atomic weights were determined. Dalton's paper was read, as we have seen, before the Manchester Literary and Philosophical Society on October 21, 1803, and was published in 1805. There is reason to believe that the numbers were obtained after the paper was read, says Roscoe (93), and inserted before its publication. Dalton gives no detailed explanation of how these actual numbers were arrived at.

In 1810, in his *New System of Chemical Philosophy*, he explains in some cases how he arrived at these weights but he had then made considerable changes in the numbers.

Roscoe very ingeniously attempts to trace the origin of these original numbers. He is struck by the clearness of perception of truth which enabled him to argue correctly from inexact experiments. "In the notable case, indeed in which Dalton announces the first instance of combination in multiple proportions the whole conclusion is based upon an erroneous experimental basis. If we repeat the experiment, as described by Dalton, we do not obtain the results he arrived at. We see that Dalton's

conclusions were correct, although in this case it appears to have been a mere chance that his experimental results rendered such a conclusion possible.''

6. The Tables of Thomson and Wollaston.—In 1810 Thomson gave in his *System of Chemistry*, a table of the equivalents for 23 acids and bases. Wollaston's Table of Equivalents published in 1814 was a decided improvement upon the preceding, as he made use of the best available work of other chemists, notably of Berzelius. Instead of taking hydrogen as the standard, he used oxygen giving it the equivalent 10.

#### WOLLASTON'S TABLE, 1814.

| Hydrogen · · · · · · · · · · · · · · · · · · · | 1.32  |
|--|-------|
| Oxygen   | 10.00 |
| Water  | 11.32 |
| Carbon   | 7.54  |
| Sulphur  | 20.00 |
| Phosphorus                                     | 17.40 |
| Nitrogen                                       | 17.54 |
| Chlorine                                       | 44.I  |
| Oxalic acid                                    | 47.0  |
| Ammonia  | 21.5  |
| Sodium   | 29.1  |
| Potassium····                                  | 49.1  |
| Magnesia                                       | 24.6  |
| Calcium  | 25.46 |
| Strontium·····                                 | 63.0  |
| Baryta   | 97.0  |
| Iron   | 34.5  |
| Copper   | 40.0  |
| Zinc·····                                      | 41.0  |
| Mercury  | 125.5 |
| Lead · · · · · · · · · · · · · · · · · · ·     | 129.5 |
| Silver   | 135.0 |

Only the most important of the equivalents are given in the above table as selected by Kopp.<sup>1</sup> Elements and compounds are given together, Wollaston declining to consider these as atomic weights and desiring to avoid the difficulties and inconsistencies of Dalton's rules.

7. The Table of Berzelius.—Between the years 1810 and 1818 Berzelius published in the Memoirs of the Stockholm Academy a number of determinations of atomic weights. His first complete table was published in 1815 and was as follows:

#### BERZELIUS' TABLE, 1815.

| Oxygen   | 100.0  |
|--|--------|
| Phosphorus                                       | 167.5  |
| Fluorin  | 60.0   |
| Carbon   | 74.9   |
| Hydrogen   | 6.64   |
| Molybdenum                                       | 601.6  |
| Wolframium                                       | 2424.2 |
| Antimony   | 1613.0 |
| Platinum   | 1206.7 |
| Mercury  | 2531.6 |
| Copper   | 806.5  |
| Cobalt·····                                      | 732.6  |
| Lead   | 2597.4 |
| Iron   | 693.6  |
| Maugauese  | 711.6  |
| Magnesium  | 315.5  |
| Strontium  | 1118.1 |
| Sodium · · · · · · · · · · · · · · · · · · ·     | 579.3  |
| Sulphur  | 201.0  |
| Muriaticum · · · · · · · · · · · · · · · · · · · | 139.6  |
| Boron  | 73-3   |
| 10.  |        |

<sup>1</sup> Gesch., 11, p. 376.

| BERZELIUS' TABLE, 1815. (Continued.)         |        |
|--|--------|
| Nitricum                                     | 79.5   |
| Arsenic                                      | 839.9  |
| Chromium                                     | 708.1  |
| Tellurium                                    | 806.5  |
| Silicon                                      | 304.3  |
| Gold   | 2483.8 |
| Silver · · · · · · · · · · · · · · · · · · · | 2688.2 |
| Nickel ·····                                 | 733.8  |
| Bismuth                                      | 1774.0 |
| Tin  | 1470.6 |
| Ziuc····                                     | 806.4  |
| Aluminium                                    | 343.0  |
| Calcium                                      | 510.2  |
| Barium                                       | 1709.1 |
| Potassium                                    | 978.0  |

In this table the bodies muriaticum, fluoricum, and nitricum are hypothetical bodies, Berzelius supposing that by union with oxygen they yielded the acids hydrochloric, hydrofluoric and nitric. These were therefore left out of the table given by Berzelius in 1826, and, furthermore, he introduced many corrections in this subsequent table. This was, then, the condition of the atomic weights and represents the extent of the knowledge concerning them when the first speculations as to the numerical relations existing between them appeared and the first hypothesis based on these was formed.

8. The Two Directions of the Work.—The knowledge of these important constants of nature led very speedily to attempts at deducing numerical regularities and relations along two lines. First there were

the efforts of Prout and Meinecke to show that these numbers were all multiples of one common unit of weight: secondly, Döbereiner blazed the way for a host of followers in discovering numerical relationships between the atomic weights of similar elements or those of the same family, and later on of the dissimilar ones.

9. Prout's Hypothesis.—In the year 1815, there appeared (1) an anonymous article upon the subject of the relations between the specific weights of bodies in the gaseous condition and their atomic weights. An abstract of this article follows and attention is especially to be drawn to the modest manner in which the author propounds his theory.

"The author of the following essay submits it to the public with the greatest diffidence; for though he has taken the utmost pains to arrive at the truth, he has not such confidence in his abilities as an experimentalist as to induce him to dictate to others far superior to himself in chemical acquirements and fame. He trusts, however, that some one will undertake to examine it and thus to verify or refute its conclusions. If these should be proved erroneous, still new facts may be brought to light, or old ones better established by the investigation; but if they should be verified, a new and interesting light will be thrown upon the whole science of chemistry."

His observations were founded on Gay-Lussac's "Doctrines of Volumes." Three tables are given: Table I containing the specific gravities of various sub-

stances, H being I, O being IO, etc. Table II gives the specific gravities of the compounds with oxygen. Table III gave the specific gravities of the compounds with hydrogen.

"I had often observed the near approach to round numbers of many of the weights of the atoms before I was led to investigate the subject. Dr. Thomson appears also to have made the same remark. It is also worthy of observation that the three magnetic metals as noticed by Dr. Thomson, have the same weight, which is double that of azote. Substances in general of the same weight seem to combine readily and somewhat to resemble one another in their nature."

"On a general review of the tables, we may notice:

1. That all the elementary numbers, hydrogen being considered as 1, are divisible by 4, except carbon, nitrogen and barium, and these are divisible by 2, appearing therefore to indicate that they are modified by a higher number than that of unity or hydrogen. Is the other number sixteen or oxygen, and are all substances compounded of these two elements?"

His other deductions have no bearing upon the matter in question.

10. Prout's Second Paper.—In 1816, Prout published another paper (2) correcting a mistake in the one just quoted. In it he expresses the following views:

"If the views we have ventured to advance be correct, we may almost consider the  $\pi\rho\omega\tau\gamma$   $\tilde{\upsilon}\lambda\gamma$  of the ancients to be realized in hydrogen; an opinion by-the-by, not

altogether new. If we actually consider this to be the case, and further consider the specific gravities of bodies in their gaseous states to represent the number of volumes condensed into one, or in other words, the number of the absolute weights of a single volume of the first matter  $(\pi\rho\omega\tau\gamma\ \tilde{v}\lambda\gamma)$  which they contain, which is extremely probable, multiples in weight must always indicate multiples in volume, and *vice versa*, and the specific gravities or absolute weights of all bodies in a gaseous state must be multiples of the specific gravity or absolute weight of the first matter  $(\pi\rho\omega\tau\gamma\ \tilde{v}\lambda\gamma)$ , because all bodies in a gaseous state which unite with one another, unite with reference to this volume."

It soon became known that the author of these papers was Dr. William Prout, a physician, and afterwards a chemical author of some prominence. His views attracted general attention and in so far as they referred to the atomic weights being multiples of that of hydrogen, and hence hydrogen being the primal element, they were looked upon with favor, more especially in England.

Hypothesis.—The hypothesis of Prout was supported by Thomson in England, and it soon had many adherents. Thomson's experiments in support of it (8) were very unsatisfactory however, and were insufficient as evidence to confirm it. It was received by some in both France and Germany, but met with strong opposition on the part of others, and was especially antagonized by Berzelius, (though he at first regarded it favorably). Berzelius gave

in 1825, a table of carefully determined atomic weights of the elements which differed in many cases widely from those used by Prout and Thomson. He also urged very strongly against the practice of rounding off the fractions of atomic weights into whole numbers. As Hoffman says: "He could not persuade himself that the numerical relations of these values betokened an inner connection of the elements nor yet a common origin. On the contrary, he was of the opinion that these apparent relations would disappear more and more as these values were more accurately determined. For him therefore, there existed as many forms of matter as there were elements: in his eyes the molecules of the various elements had nothing in common with one another save their immutability and their eternal existence."

Yet in 1827, (10) Gmelin gives in two parallel columns the atomic weights of Berzelius, with their fractions (oxygen being taken as 100), and the same weights rounded off into the whole numbers (hydrogen being the standard).

He adds: "It is surprising that in the case of many substances the combining weight is an integral multiple of that of hydrogen, and it may be a law of nature that the combining weights of all other substances can be evenly divided by that of the smallest of them all."

12. Examination of the Subject by Turner.—In 1829, (11) Turner, who was then an adherent of the hypothesis, began a revision of the work of Thomson. Later, in 1832, he was specially delegated by the British

Association to inquire into and report upon this question. The basis of the work of Thomson had been the determination of the atomic weight of barium. This Turner critically revised and decided that Thomson's work was erroneous and that of Berzelius correct. In Turner's report in 1833 (12) he gave up the support of the hypothesis.

- 13. Penny's Results.—In 1839 (13) Penny attacked this question from a different standpoint. If the atomic weights were represented by whole numbers, then their differences should also be integers. In a series of experiments upon potassium chlorate and potassium nitrate, he showed that this was not the case. He withdrew his support from the theory and thus, in its home, it was losing ground. But the failing theory was destined to be revived and brought vigorously to the front again in the laboratories of France.
- 14. Dumas' Adhesion to Prout's Hypothesis.—At this time a number of excellent workers were busied upon the revision of the atomic weights. Among them may be mentioned Pelouze, Marignac, Erdmann, Marchand, Svanberg, Peligot, and others. In many cases the numbers obtained by them did not differ greatly from whole numbers, and influenced by their work, as well as by his own numerous determinations, Dumas, in 1840, revived the hypothesis of Prout. His views were strengthened in 1842 (14) by the re-determination of the ratio of carbon to hydrogen, carried out by his pupil Stas and himself, which was shown to be almost exactly

- 12:1. This was followed by his work upon oxygen and nitrogen, giving their ratios as very nearly 16:1 and 14:1 respectively.
- 15. The Extension of the Hypothesis.—The atomic weight of chlorine had proved a great stumbling block to the supporters of Prout's hypothesis. No revision changed it materially from 35.5. Copper and lead and some other elements gave similarly troublesome fractions. To overcome this Marignac suggested in 1844 that half the atomic weight of hydrogen be used as the unit and thus bring chlorine within the list of integral multiples. The idea was taken up by Dumas with enthusiasm, but he found it necessary to go a step further and take one-fourth the atomic weight as the unit. This was in 1858 and will be spoken of later. Erdmann and Marchand are to be classed among the Proutians at this time, and indeed, according to Berzelius (9.b) specially exerted themselves to find confirmatory evidence for the theory.
- 16. Prout's Later Views.—It is interesting to quote from a later work of the author of this hypothesis (3, p. 110) and see how his views stood the stress of the heavy conflict waged for and against them.

"It may be observed that we have spoken as if the atomic weights of bodies were related to one another by multiple and were all multiples of some common unit. Now this opinion has been maintained by some, while it has been denied by others, who, admitting that multiples in weight are necessary to the union of similar molecules,

both chemically and cohesively, will not admit that multiples are necessary to the union of dissimilar molecules. The matter is one which in the present imperfect state of chemistry, can hardly be determined by experiment; for what with the difficulty or rather impossibility of procuring bodies in a perfectly isolated form, and the unavoidable imperfections of all chemical processes, we can scarcely hope to approach within the necessary limits of precision."

17. The Views of Meinecke. — Meinecke has been mentioned by some as having, independently of Prout, announced the same views at about the same time. This may have arisen from the fact that Ostwald, in the first edition of his "Allgemeine Chemie," refers to Meinecke's "Chemische Messkunst," which was published in 1815. The proper citation is given in the second edition of this work and refers to a period three years later. The citation (4) is as follows:

"It is noteworthy that the number of hydrogen is a divisor of the remaining stoichiometrical numbers. That this should be absolutely correct in the case of those simple bodies which have been most accurately determined, and that in the case of most of the others it should accord as nearly as could be expected for difficult analyses, is certainly not to be looked upon as an accident, but rather it is to be assumed that the numbers of all simple bodies, and consequently of all compound substances, form integral multiples of the value of hydrogen. There are also deeper theoretical grounds to speak for

this. This combined with the calculations based on volumes furnish the chief means for the accurate determination of these chemical magnitudes."

18. Prout's Views as to the Constitution of Matter.

—It is pertinent to the subject to append here Prout's views as to the constitution of matter.

"Although we have thus rendered it probable that the molecules of bodies, considered at present as elementary, are immediately compounded of many others, more or less resembling them; yet it is obvious that there must be a point at which these and other elements exist in a primary and ultimate form, and beyond which, if the elements can be supposed to be subdivided, they must become something altogether different. In this respect, therefore, the views we have advanced accord greatly with the views at present entertained, and the only respect in which our views differ is in supposing that the self-repulsive molecule as it exists in the gaseous form, does not represent the ultimate molecule, but is composed of many sub-molecules. With respect to the nature of the sub-molecules of these bodies, which we at present consider to be elements, as for instance of oxygen, they may naturally be supposed to possess the most intense properties. Indeed such sub-molecules may be imagined to resemble in some degree all imponderable matters, heat, etc., not only by their extreme tenuity, but in other characters also; and this very intensity of property and character may be reasonably considered as one, if not the principal reason, why they are incapable of existing in a detached form.

19. Early Numerical Relations.—Leaving now the hypothesis of Prout, let us consider other numerical relations among the atomic weights than their divisibility by some common factor.

Before the atomic theory was formulated by Dalton, we have Richter's table of equivalents (in 1798) exhibiting the mass relations when an acid is neutralized by certain bases. Richter was very strongly of the opinion that his constants were subject to special laws, particularly if arranged in the order of their magnitude.

Strictly speaking, the first notice of numerical relations existing between the atomic weights of the elements, apart from the question of their being multiples of the weight of hydrogen, was that which Prout deduced from his table, namely, that they were all divisible by four, except three, which were divisible by two. Of course, Prout's table was very crude and imperfect.

20. The Triads of Döbereiner.—It is to Döbereiner that the credit is due for drawing attention to the first striking regularities. He observed the fact that certain related elements occurred in threes, the central one having a mean atomic weight and mean properties between the other two. These were called the Döbereiner Triads. The first publication concerning them did not come from Professor Döbereiner himself, but from a letter of Professor Wurzer's, describing the work of Döbereiner at Jena (5). He says that Döbereiner, working upon celestite, found

the stoichiometrical value of strontium to be 50. This is the mean of calcium, 27.5, and barium 72.5, (the then accepted atomic weights). Hence, for a moment, he questions the independent existence of strontium. Still more remarkable is the fact that the specific gravity of strontium sulphate is the mean of calcium sulphate and barium sulphate. He was led to believe celestite to be a mixture of anhydrite and heavy spar.

A little later (6) Döbereiner published a brief paper bearing upon this subject. In it he says:

Noteworthy relations are revealed when one examines the stoichiometrical values of the chemical elements and compounds arranged in series.

- 1. Those most often found in plants have the smallest values and are the most abundant. The highest values are less widely distributed.
- 2. Those corresponding in many physical and chemical properties, as iron, cobalt and nickel, have almost the same stoichiometrical value.
- 3. Compounds which have like equivalent numbers are also most alike in chemical constitution.
- 21. Döbereiner's Resume of His Law.—For nearly a decade there is silence upon this subject. Döbereiner's next publication seems to have been called forth by the new and accurate atomic weight determinations of Berzelius in 1825. He writes (7) of his having prophesied in his lectures that perhaps the atomic weight of bromine would be the arithmetical mean of those of chlorine and iodine and rejoices in the confirmation of

this by the determination of Berzelius. Bromine had just been discovered. He had also twelve years earlier placed strontium as very nearly the arithmetical mean between calcium and barium, and sodium between lithium and potassium. For the group of phosphorus and arsenic the middle factor is lacking. If sulphur, selenium and tellurium belong together, which is to be assumed from the fact that the specific gravity of selenium is the mean of the specific gravities of sulphur and tellurium, then selenium is the mean factor in the matter of atomic weights.

Fluorine, he says, does not belong to the same group of salt-formers as chlorine, etc., but doubtless to one which bears the same relation to this group as the alkalies to the alkaline earths. He further attempts to show in this grouping the intensity of the chemical attraction. Hydrogen, oxygen, nitrogen and carbon, he says, seem to be isolated, and the fact that nitrogen is the mean between oxygen and carbon cannot be considered as meaning anything since no analogy exists between these elements.

The third member is lacking between boron and silicon, beryllium and aluminium, yttrium and cerium. Magnesium stands quite alone. Iron and manganese have chromium as their middle factor. Other possible groups are mentioned, but he hesitates to express his opinion regarding several where the properties are poorly determined and the analogies indistinct.

The important fact is that he recognized it as a law of nature that the elements occurred in groups of threes, the middle factor being the arithmetical mean of the other two in atomic weight and in properties.

- was taken up by other chemists who tried, as the knowledge of the elements increased, to complete the unfinished triads and to observe other analogies. These triads played quite an important part in Gmelin's Hand Book of Chemistry, the most influential text-book of chemistry during the second quarter of this century. With this exception not much notice was taken of them.
- 23. Berzelius on Such Numerical Relations. In 1845, Berzelius writes (9.b): "On examining the tables of atomic weights it will be found that many bodies have an equal or almost equal atomic weight, as for instance, chromium and iron, nickel and cobalt; platinum and iridium; gold and osmium; many have also a weight twice as large as the others, for instance, silicon and boron; tungsten and molybdenum; magnesium and lithium, etc., the atomic weights of oxygen and sulphur, selenium and tellurium are in the ratio of 1, 2, 5 and 8; add to this those which seem to be multiples of the equivalent of hydrogen; thus it is seen that between bodies of a certain similarity of properties, certain weight relations obtain. It could easily happen that a revision of these numbers would separate them further from one another or from their seeming relations. and it is therefore useless at present to speculate upon such relations. They could easily lead to false assumptions."



## CHAPTER II.

DUMAS AND THE PERIOD FROM 1850 TO 1860.

24. Slow Development of the Triads.—For more than twenty years little was added to the work of Döbereiner and no new ideas were developed. This was in part due to imperfections in the determinations of the atomic weights and ignorance as to whether they should be written as had been done by Berzelius, or many of them doubled as was done by Gerhardt.

Further, the whole question of atomic weights was in much doubt and numerical speculations concerning them would have had little meaning during this period. The first high wave of hope and expectancy following upon the introduction of the idea of atoms and the tables of their weights was succeeded by a corresponding period of doubt and difficulty. Graham made no distinction between the atomic weights of Dalton and the equivalents of Wollaston, and much later Laurent devotes several pages to discussing the merits of the various terms: equivalents, proportional numbers, and atomic weights.

25. Dumas' Address before the British Association.

—The first to take up once more the dropped thread was Dumas (16). He had devoted his chief energies to atomic weight determinations and had erected a lasting monument to himself in his determination of the atomic weights of carbon and the ratio of hydrogen and oxygen in water, besides a number of other determinations. In 1851 he delivered a lecture before the British Association at Ipswich, which aroused the greatest interest

among chemists, and with this lecture began the most prolific decade in this style of research down to the present.

This address of Dumas' was made without notes and the reports of it lack completeness. It seems to have been drawn out in a discussion following a report presented by Faraday. The larger portion of it was gathered together with some later papers of his and appeared in a connected form in 1859. In this address he drew attention to the triads of Döbereiner, without, however, mentioning this author's name, and suggested that in a series of bodies, if the extremes are known, then by some law the intermediate bodies might be discovered, and said that a suspicion arose as to the possibility of the intermediate body being composed of the extremes of the series and thus processes of transmutation might be hoped for. In so far as concerned the composite nature of the intermediate elements he but reiterated the early suspicion of Döbereiner. He then alluded to the possibility that such metals as were similar in their relations and could be substituted one for the other in certain compounds, might also be found transmutable one into the other. Dumas spoke of the idea of the ancients as to the transmutation of metals and their desire to change lead into silver and mercury into gold; but these metals do not appear to have the requisite similar relations to render these changes possible. He then passed to the changes of other bodies, such as the transmutation of the diamond into black lead under the voltaic arc, etc.

After elaborate reasoning and offering many analogies

from his stores of knowledge as to chemical analysis and reactions, Dumas expressed the opinion that the law of the substitution of one body for another in groups of compounds might lead to the transformation of one group into another at will; and that we should endeavor to devise means to divide the molecules of one body of one of these groups into two parts, and also the molecules of a third body, and then unite them, and probably the intermediate body might be the result.

The facts of associated occurrence in nature of such bodies as cobalt and nickel, chlorine, bromine and iodine were taken as possible evidence in favor of transmutation.

- 26. The Effect of Dumas' Address.—These views of Dumas led to a number of experiments by Despretz, and a lively discussion between these two chemists some years later. This will be referred to at the proper time. A more immediate result followed his taking up of the triads of Döbereiner and pointing out additional regularities of that kind. This was a fruitful field and a strangely fascinating one to a man who once enters upon it. In the next few years we have a number of well-known chemists engaged upon this work.
- 27. Faraday's Views.—It is perhaps well to show by a quotation from Faraday (20) how this conservative and distinguished worker looked upon the opinions advanced by Dumas. In his lecture upon chlorine, bromine and iodine (pp. 158, 159, 160), he says:

<sup>&</sup>quot;When we come to examine the combining powers of

the three, as indicated by their respective equivalents or atomic weights the same mutual relation will be rendered evident. This circumstance has been made the basis of some beautiful speculations by M. Dumas—speculations which have scarcely yet assumed the consistence of a theory, and which are only at the present time to be ranged among the poetic day dreams of a philosopher: to be regarded as some of the poetic illuminations of the mental horizon, which possibly may be the harbinger of a new law."

He then considers the triads of salt-makers, of alkalies, of alkaline earths, and the sulphur triad, and continues: "Thus we have here one of the many scientific developments of late origin, which tend to lead us back into speculations analogous with those of the alchemists. Already have we seen that it is possible for one body to assume, without combination, two distinct phases of manifestation, therefore such of the so-called elements as are subject to allotropism, are not the unchanging entities they were once assumed to be; and now we find, after our attention has been led in the direction, that the triad of chlorine, bromine, and iodine not only offers a well-marked progression of certain chemical manifestations, but that the same progression is accordant with the numerical exponents of their combining weights. We seem here to have the dawning of a new light, indicative of the mutual convertibility of certain groups of elements, although under conditions which as yet are hidden from our scrutiny.".

- 28. The Ascending Series of Kremers.—One of the first to follow in the footsteps of Dumas was Kremers (18) who pointed out the existence of certain regularly ascending series among the elements. Thus, when we take certain analogous non-metals as 0=8; S=16; Ti = 24.12; P = 32; Se = 39.62, etc., we see that there is a regular difference of eight between them. Now many metals lie in between these as Mg = 12.07 between O and S; Ca = 20 between S and Ti; Fe = 28 between Ti and P, etc. Divide these by four and the non-metals give an even number and the metals an uneven. A fundamental element with the atomic weight four can therefore be assumed. This multiplied by an even number gives a non-metal, by an uneven it gives a metal. In salts, then, looked at from a dualistic point of view, the acid is an even multiple of four and the base is an uneven one, and this, in the opinion of the author, lends strength to his hypothesis of the fundamental element. Kremers gives a table of these non-metals, their atomic weights, and their factors (multiples of 4) and also the metals falling in the intermediate spaces. To this latter fact he seems to attach a good deal of importance. He includes among his non-metals several bodies now regarded as metals.
- 29. The Triads of Kremers.—In later communications (29), he follows up the old idea of triads and of the probable composite nature of the intermediate elements. From his examination of various compounds he deduces the law: "If two different bodies mix and form a

homogeneous whole the intensity of the physical properties of these mixtures is as a rule modified."

By this he means that instead of the product having exactly intermediate properties, these properties are modified at all temperatures save one. For instance, in examining the question whether the solubility of the salts of the intermediate member of a triad form the means of the solubilities of those of the extremes, he finds this to be true for a certain definite temperature only. He was of the opinion that the differences observed in the atomic weights of middle members of triads from the calculated were due to the temperature at which the determinations were made, and that only at one temperature could exactly agreeing compounds be obtained.

From the consideration of compounds this law is transferred to elements, and he examines a number of the properties in connection with the triads. This was an attempt at placing the doctrine of triads upon a firm experimental basis, if such a thing were possible. Döbereiner had suggested it as holding good for some elements, but did not know whether it could be extended to all. It had been extended to many, but there were still a number of doubtful ones. Kremers united some of the triads into what he called conjugated triads. His study of the properties led him to doubt the constancy of the atomic weights.

His theory of conjugated triads may be explained a little more in detail. One of these ran in this way:

$$Li = 7,$$
  $Na = 23,$   $K = 39.$   $Mg = 24,$   $Zn = 40,$   $Cd = 112.$   $Ca = 40,$   $Sr = 87.5,$   $Ba = 137.$ 

In these triads we have the following proportions: Li: Na: K as 7:23:39 as Li: Mg: Ca.

This close agreement is not found in every case, however. It was claimed that there were eight of these conjugated triads, and each twenty-seven elements can be arranged in space in the form of a cube. Of these cubes there are again three or a triad; one positive, one negative and one intermediate. The number of the possible elements is then a power of three, probably three raised to the fourth power.

Kremers at first thought that this cubic triad represented the natural arrangement of the elements. This view he gave up later (1863), and with it the doctrine of the triads in the strict sense.

30. Gladstone's Arrangement in the Order of their Atomic Weights.—In 1853 Gladstone (21) published an article on the relation between the atomic weights of analogous elements. In this he arranged the elements in the order of their atomic weights, using the numbers given in Liebig's Jahresberichte for 1851. A few years later this method of arranging them brought out the main features of the natural law, but the numbers used by Gladstone are too faulty to show any noteworthy regularity. Still it is interesting to note that he is the first to arrange them in this order. He observed nothing striking in these numbers except the number of

them congregated around 28 and 52, and that there was only one between 80 and 99, and then followed a group of four.

Prof. DeMorgan helped him to calculate the probability of such occurrence being accidental, and found that the odds were 250 to one against the same number occurring six times in the sixty elements. Taking the elements next by groups, as given in Gmelin's Handbook, Gladstone found the numerical relations to be of three kinds.

- 1. The atomic weights of analogous elements are the same.
- 2. The atomic weights of analogous elements are in multiple proportions.
- 3. The atomic weights of analogous elements may differ by certain regular increments.

In the first class fall Cr, Mn, Fe, Co, Ni with atomic weights approximating 28; Pd, Rh, and Ru approximating 52: and Pt, Ir, and Os approximating 99.

In the second class we see the platinum group double the palladium group, and gold double platinum. Again he gives O = 8 and S = 16; and B = 10.9 and Si = 21.3 as examples. A group consisting of Ti, Mo, Sn, V, W, and Ta is cited as having atomic weights which are all multiples of 11.5.

In the third class we have elements with intermediate properties occupying intermediate positions. Li, 6.5; Na, 23; K, 39.2.

The first kind of analogy he compared with allotropism if that were carried out through all the compounds of an element. The second is to be compared with polymerism in organic chemistry.

The third is analogous to the homologous series in organic chemistry.

He regarded the doctrine of triads as to some extent a natural law, but the existence of these triads was to him an unsolved problem.

31. The Homologous Series of Cooke.—In the following year Professor Josiah P. Cooke (22) published a very detailed study of these numerical relations. He thought that the doctrine of triads as given by Dumas was only a partial view of the subject, since these triads are only parts of series similar in all respects to the homologous series of organic chemistry, in which the differences between the atomic weights is a multiple of some whole number. In so far as he pointed out that these triads broke up natural groups of elements, he struck a fatal blow to the doctrine of triads.

All the elements, he said, may be classified into six series, in each of which the number whose multiples form the differences is different and may be said to characterize the series. In the first it is nine, in the second, eight, in the third, six, in the fourth, five, in the fifth, four, and in the last, three. The elements are further arranged in series according to the strength of their electro-negative properties, or in other words, as their affinities for oxygen, chlorine, sulphur, etc., increased, while those for hydrogen decrease, as we descend. He found the difficulty with most of the classifications, exist-

ing at that time, to be that they were too one-sided, based upon one set of properties to the exclusion of others. If there were any fundamental property common to all elements, the law of whose variation was known, this might serve as the basis of a correct classification. Professor Cooke laid special stress upon the correspondence of his grouping with the homologous series of organic chemistry.

The elements of any one of the six series form similar compounds and produce similar reactions; moreover they resemble each other in another respect in which the members of the organic series do not, their crystalline forms are the same, or, in other words, they are isomorphous. As one general symbol will express the composition of the whole organic series, so a simple algebraic formula will express the atomic weight, or, if you may please so to term it, the constitution of a series of elements.

In the first series the atomic weights gradually increase from oxygen downward and admit of a general expression, which is 8 + n9. This series is comparable to the formic acid series. For the next series the generic formulas are 8 + n8 and 4 + n8. Thus this series is divided into two sub-series, in which there are marked analogies. There seems to be no proof of isomorphism between the sub-series.

For the next or six-group the formula is 16 + n12. Oxygen is placed at the head of each one of these three groups because "its atomic weight seemed to be the nucleus of all three." In other cases also we find the

same element occurring in more than one group. The five-series is the shortest of them all, containing only three elements. Its formula is  $6 + n_5$ . The four-series is much the largest of all, containing what are known as the heavy metals. This is divided into two sub-series with the two formulas  $4 + n_4$  and  $2 + n_4$ . The three-series and last is composed of hydrogen and the alkalies, only three of which were known at that time. The formula here is  $1 + n_3$ .

Cooke caught a glimpse of one great truth, and that was that we must not merely separate out here and there so-called related elements, but must grasp the fact that there is a relationship even between the apparently dissimilar. He says that one of the most remarkable facts brought out by his system of tabulation is the "affiliation of the series." "Many of the elements, while they manifestly belong to one series, have properties which ally them to another." He concludes, that this table shows that the chemical elements may be classified in a few series similar to the series of homologues of organic chemistry; secondly, that in these series the properties of the elements follow a law of progression; and finally that the atomic weights vary according to a similar law, which may be expressed by a simple algebraic formula.

32. Kotikovsky and the Compound Nature of the Elements.—In this same year (1854), Kotikovsky (23) took up the idea of the compound nature of the elements suggested by Dumas, and attempted to prove the truth

of this by a singular mode of reasoning and without experimental proofs. It has not been possible to get at the original article, nor has it been deemed necessary to make a very extended search for it. Following the lead of Priestley and the phlogistic chemists, he assumed the presence of hydrogen in all combustible bodies. He develops a simple appearing system of chemistry in which there are no troublesome exceptions to his rules, because all facts which do form exceptions are stated otherwise and made to accord. He gives no proof of how he found these to be different from what is commonly accepted. The following example of his mode of reasoning will suffice: "Water = 18 can not contain oxygen = 32 because no part can weigh more than the whole."

33. Low's Theory as to the Composition of the Elements.—Low (25) held that hydrogen and carbon were the original constituents of many of the elements. Thus he regarded N as C<sub>2</sub>H<sub>2</sub> and O as CHH, etc. As experimental evidence he offered the fact that potassium or sodium melted under rock-oil became oxidized, and this he regarded as a making of oxygen.

Since hydrogen and carbon (atomic weight 6) had at that time lower atomic weights assigned them than any other elements, and since they were capable beyond all the others of entering into combination with one another, he assumed that all elements are composed of the two. Or, to state the proposition more generally, all bodies may be derived from hydrogen and carbon or from the

principles, elements, or matter, of which hydrogen and carbon are themselves formed.

He examined in detail the various elements and endeavored by appeal to experiments and analogies to show how they were made up of one another and all composed of hydrogen and carbon. The relations existing among organic substances were adduced in support of the theory.

Further, he criticised the reasons for holding certain bodies to be elementary and a demonstration was given of how all elements might be built up of, say, two bodies, A and B. Of the nature of the ultimate atoms or particles we "know and can know nothing." "We infer that they have weight and extension." "We cannot conceive a body to have weight and extension, and the parts of which it is formed to be destitute of weight and extension, however far we suppose the division to be carried." The conception of Boscovich of the atom as infinitesimally small and hence a mathematical point, or of the philosopher as merely a resisting point, and hence all matter to be but a system of forces is not the idea of the chemist who regards it as a "particle of matter."

Low believed that it was unjust to regard bodies as simple or elementary merely because we are unable to decompose them by the means at our disposal. Induction and analogy should be relied upon as well as experiment. Without them experiment would fail to conduct us to the discovery of natural laws. "It would be justice to regard a body as compound when we are not able to prove it to be simple." Many things show that the two arbitrary classes, elements and compounds, are not to be

divided by so wide a chasm as a "distinct corpuscular constitution."

"Davy, in the early period of his chemical inquiries, was conducted to the opinion that sulphur and phosphorus, which give off hydrogen under the influence of voltaic action, might be compound. He even expressed the opinion, that all simple bodies might be compound and resoluable into hydrogen and some unknown base. He never, however, pursued his own hypothesis to its consequences, and at length he seems to have abandoned it altogether."

34. The Extension of the Triads by Lennsen.-Lennsen, in 1857, (26) returned to the doctrine of the triads and is almost the last one to attempt the development of this line of speculation. He endeavored to extend the triads to all of the elements, grouping them by their physical and chemical characteristics. He formed, in all, twenty triads, thus including the sixty best known elements. Mercury formed the uniting member, appearing in the tenth and again in the twentieth triad. The first ten triads contained the non-metals and acid-forming metals; those from eleven to twenty contained the metals. He noted a further intimate relationship between the triads. Thus, for each three triads we have the middle members forming a new triad, and, therefore, the three triads formed what he called an enneade. This is, of course, a very similar idea to the conjugated triads of Kremer's. He saw, however, that the division into triads was not entirely satisfactory. The middle member did not always present in every respect the intermediate characteristics. He then suggested a division into diads with the third member forming a link or binding member. The triads, K, Na, Li; Ba, Sr, Ca; Mg, Zn, Cd; became diad K, Na, and link Li; diad Ba, Sr, and link Ca; diad Mg, Zn, and link Cd, and so on for the others. He laid especial stress upon the analogous salts of these diads crystallizing with the same amount of water.

Other properties, as the color of the salts, color given to flame, etc., were also brought to bear in effecting this division.

35. Elaboration of the Homologous Series by Dumas.

-In the latter part of the year 1857, Dumas (27) took up again the subject of the numerical regularities of the atomic weights and this time not from the point of view of the triads but of the homologous organic series. He made use of the formula devised by Cooke, a + nd. The facts that organic radicals are not always produced by addition but sometimes by substitution and again that there are certain series of radicals where the fundamental molecule itself changes as well as the bodies added to or substituted in it, are especially emphasized. In comparing the equivalents of the elements he noted that the halogens do not form a simple progression. The relation between their equivalents is, however, exhibited by the scheme a, a + d, a+2d+d', 2a+2d+2d'. Thus F = 19; Cl = 19 + 16.5; Br = 19 + 2(16.5) + 28; I = 2(19) + 2(16.5) + 2(28). And so for the nitrogen group; N = 14; P = 14 + 17; As = 14 + 17 + 44; Sb =

14 + 17 + 88; Bi = 14 + 17 + 176. Similar series are given for C, B, Si, and Zr; as well as for Sn, Ti, and Ta. For the oxygen group we have the series a, 2a, 5a, 8a, or a, a + d, a + 4d, a + 7d. Taking the latter as preferable from analogy, O = 8; S = 8 + 8; S = 8 + 32; T = 8 + 56. A common difference of eight also connects the following: Mg = 12; Ca = 12 + 8; Sr = 12 + 32; Ba = 12 + 56; Pb = 24 + 80. The following have a common difference of sixteen: Li = 7; Na = 7 + 16; K = 7 + 32. Mo, W, Cr, and V form a similar series with the difference 22.

**36.** Double Parallelism of Dumas.—A few months after this Dumas brought out his idea of double parallelism. He made the following comparison:

$$N = 14$$
  $P = 31$   $As = 75$   $Sb = 122$   $F = 19$   $Cl = 35.5$   $Br = 80$   $I = 127$ 

On adding 108 to the number for nitrogen we get that for Sb, and on adding it to F we get I, and so the addition of 61 gives us respectively As and Br. These facts teach the propriety, he says, of arranging the metals in series that shall show a double parallelism, for such a classification brings to view the various analogies existing between these elements. In fact, when arranged by natural families, each of the elements is in proximity to two others, belonging to two related families; and these related families occupy the two lines next to that containing the metal selected for comparison. Finally each metal is surrounded in such a table by four others, which are united to it by analogies of different kinds and more or less close.

37. Dumas' Views as to Compound Nature of the Elements.—In a further communication he draws this comparison between the elements and the other bodies in nature. The compounds which the three kingdoms offer for our study are reduced by analysis to a certain number of radicals which may be grouped in families. Secondly, the characters of these families show incontestable analogies. But the radicals of mineral chemistry differ from the others in that if they are compound they have a stability so great that no known forces are capable of producing decomposition. The analogy authorizes the inquiry whether the former may not be compound as well as the latter. It is necessary to add, he says, that the analogy gives us no light as to the means of causing this decomposition and if it is ever to be realized it will be by methods or forces yet unsuspected.

In 1859, Dumas (34) collected and published in one article the more important parts of his work upon the numerical relations of the atomic weights, laying special stress upon the probably composite nature of the elements.

38. The Dumas-Despretz Controversy as to the Composition of the Elements.—This idea of the composite nature was combatted by Despretz (35), who performed a number of experiments to determine, if possible, whether the elements could be looked upon as varying modifications or condensations of one and the same material or whether they were compounds of unknown constituents. For instance, he found that copper sul-

phate gave at the beginning and end of its electrolysis the same body, copper, with the same characteristics. So too by fractional precipitation of copper with hydrogen sulphide or with sodium carbonate he got only one substance. The same was true of lead nitrate when fractionally precipitated by means of sodium carbonate. Electrodes were sunk in melted lead and the metal examined at the positive and negative end. Both were identified with ordinary lead. Zinc, on being fractionally distilled, yielded zinc only and the same was true of chlorine. These suffice to give the character of his experiments. He thought he could conclude that the elements consisted of peculiar elementary material, unchangeable in its nature and properties and that they were by no means the same matter in different molecular condition.

Dumas replied that Despretz's methods were inadequate to solve this question and that no just conclusions could be drawn from them.

Despretz defended the correctness of his researches. He volatilized Cu, Bi, and Ag in a stream of hydrogen by the white heat of a furnace and more rapidly by a strong galvanic current and showed that these volatilized metals gave the same compounds as before. He also showed that Fe, Cu, Bi, and Ag gave out no hydrogen nor other gas at a white heat.

It does seem as if this work of Despretz was one of supererogation as Dumas had distinctly stated in his speculations upon the composite nature of the metals that their decomposition, if ever accomplished, would be by means and methods yet unsuspected. Dumas' reply to such criticism as these was a very easy one.

39. Pettenkofer's Group Differences.—Pettenkofer (30), in pursuing this subject of the regularities in the weights, first criticized the doctrine of triads. That the equivalent of a body, he says, should form a mean between two very similar bodies is certainly only something accidental. One can compare F, Cl, and Br as well as Cl, Br, and I and then the mean relation does not appear.

He maintains that a remarkable relation does appear, however, when one examines the numerical differences between certain natural groups of elements, these differences seeming to be nearly multiples of one and the same number. He examines the alkalies, alkaline earths, chromium group, and sulphur groups and finds the number to be eight. Thus  $\text{Li}=7+2\times8=\text{Na}+2\times8=\text{K}$ . Another number, five, is found for the halogens and for the C, B, Si group; also by the group N, P, As, and Sb it seems to be made up of 5 and 8.

He regards the occurrence of these differences approximating eight as too frequent to be accidental, thus making use of the style of argument which he had rejected in the case of the triads. By taking eight as the difference and using some member of each group as the unit he calculates out the atomic weights for the group. A table is given in which the atomic weights are thus calculated and compared with the observed weights and the differences are also tabulated. He did not think that the fact that this number eight was the one then regarded as the atomic weight of oxygen should have any meaning.

## 40. Comparison of Elements with Compound Radicals.

—He further compared the elements with the organic radicals and thought that the metals would come to be regarded as compound radicals. He thought the whole matter could be stated briefly thus:

- 1. The equivalents of the inorganic elements, which form natural groups, show among themselves such constant differences as the equivalents of organic compound radicals which belong to natural groups.
- 2. The simple inorganic elements can therefore be regarded from the standpoint of the compound organic radicals.

The difference-numbers are not always the same number or its multiples but are to be looked upon as built up of two numbers and their multiples, thus the 18 of the nitrogen group is  $2 \times 5 + 8$ .

Pettenkofer made a claim for priority that he had delivered a lecture upon these difference-numbers one year before Dumas' brilliant address. More work was needed upon the atomic weights to enable him to complete his confirmation of the supposed law. He had applied to the Royal Society of Munich for aid which had been denied him and he had therefore given the work up. This claim was justified so far as his ideas concerning difference-numbers and compound radicals were concerned. The trend of the work, however, was different, and Pettenkofer's was almost unknown while the influence of Dumas' speculations was widely felt.

41. Odling's Triads.—Odling (28) should be men-

tioned as another of the followers of the doctrine of triads. He made these the basis of a system of the elements which he arranged according to their physical and chemical characteristics, into natural families. In several cases he included more than one triad in the same family. These natural groupings of the elements were based upon the properties of the elements other than the atomic weights and may be regarded as a development of the families already recognized. For this all properties must be considered. Two elements forming a large number of compounds of analogous composition with marked similarity of properties must be grouped together. If a marked general accordance is found a discrepancy in some particular property is to be overlooked. This grouping requires a careful and thorough discussion of the properties as far as they are known. Such a classification is likely to be upset by increased knowledge of the proper-The groups are mainly triads though several are The intermediate terms of the triads are possessed of intermediate atomic weights and properties. The mean differences or increments of atomic weights in the different groups were noted. He spoke of the larger groups as triads with which were associated analogous elements having atomic weights approximately one half that of the first member or double that of the last member of the triad. Sometimes there occur what he calls twin elements.

42. Mercer's Comparison with the Organic Radicals.—Mercer (31), in a paper before the British Association, pointed out many numerical relations and

differences between groups of elements. He carried out more fully the comparison with the organic radicals. In the alkaline group, Li = 7 corresponds to H; Na = 23 corresponds to  $C_2H_3$ ; K=39 corresponds to  $C_4H_6$ . He made use of some of the difference-numbers of Pettenkofer and also noted that the difference between the nitrogen group and the halogens is 5; N=14, F=19, &c. Hence F=5+N; Br=5+As. Again  $4_2=0$ ;  $4_3=Mg$ ;  $4_4=S$ ;  $4_6=Ca$ ;  $4_{10}=Se$ ;  $4_{11}=Sr$ ;  $4_{16}=Te$ ;  $4_{17}=Ba$ ; 4+3=Li;  $4_6+3=Na$ ;  $4_9+3=K$ . Let us take as a further example one of his groups. C=6 or 5+1=6=ab+b=CH+H.

B = 5 + 6 = 11 or  $5_2 + 1 = 2 \text{ ab} + b = 2 \text{CH} + \text{H} = \text{Methyl}$   $Si = 5_3 + 6 = 21$  or  $5_4 + 1 = 4 \text{ab} + b = 4 \text{CH} + \text{H} = \text{Ethyl}$  $Zr = 5_5 + 6 = 31$  or  $5_6 + 1 = 6 \text{ab} + b = 6 \text{CH} + \text{H} = \text{Propyl}$ 

A number of such groups are given. There is appended what is called a table of the Atomic Parallels, which is the first attempt at representing the atomic weights in a diagram. The atomic weights from the ordinates. Then the oxygen group is represented by three straight lines, the first beginning at 8 and ending at 16, the second beginning at sixteen and going to 40, the third beginning at 40 and going to 64. For the magnesium group these lines began at 12, 20, 44 respectively and ended at 64. The foot notestates: "oxygen and magnesium groups, showing the steps or differences between each member; they are parallel except that Mg is raised up 4. Similar parallels are given for the nitrogen and chlorine groups." From his tables of the groups compared with the organic

radicals Mercer deduced a general formula as an expression for the atomic weights of single groups of elements; as mx or mx + y, where x and y are constant for the same group.

43. The Revision of the Atomic Weights by Cannizzaro.—In 1860 and the year or two following, M. Carey Lea published a number of articles bearing upon the numerical relations of the equivalents. As they were continuations of the same general search, though in a rather scattering fashion, for some law or laws underlying these relations they will be mentioned together. Preliminary to this mention, however, it must be stated that the atomic weights were now in a much more satisfactory condition. As has been seen from the quotations already made from various workers, there was very little uniformity in the usage as regards these numbers. Some took one authority, some another, and the numbers differed widely and were quite far removed in many cases from those at present in use. So great was this confusion and discord that a meeting, international in character, was called in 1860 to meet at Karlsruhe to come to some agreement with regard to their definite and fixed representation. The unitary theory represented by Cannizzaro gained much ground yet it was evident that no full agreement could be arrived at.

Cannizzaro's views afterwards prevailed. They were based on the conceptions of Avogadro, Gerhardt and Regnault and withstood all criticism. His idea of atoms was the smallest portion of an element which enters into

a molecule of its compounds and his table of the atomic weights was the first that gave such approximately correct values as admitted of an insight into the underlying laws.

44. Lea uses the Atomic Weight Differences.-Lea began his first paper with the remark (39): "Increasing accuracy in the determination of the chemical equivalents of the simple bodies seems to destroy more and more the numerical relations once supposed to exist between the equivalent numbers of certain series of elements nearly related to each other by their properties. Yet it can be demonstrated that such relations exist." The first part of Lea's work referred to the numerical differences between the atomic weights of the elements of the same group or family. Thus he formed a descending series begining with Sb 120 and having a regular decrease of 45. In this way he hit very nearly the atomic weights of the other elements of the group. But he did not stop there going on to a number of negative equivalents and remarking upon the cases where they happened to coincide with known positive atomic weights. He found the difference between the elements of the mercury group and so also for the magnesium group. The difference 45 is found between the two groups of the platinum metals. Between a number of elements, not easily classed together, he observed that the difference was nearly twice 44. And so for certain acid-forming elements, as Sn, Ti, Mo, &c., a variety of relations are brought out by adding or subtracting 44.

The elements C, B, and Si are united as follows: (C)

12, (B) 11, (Si) 21 = 44. Here he is misled by a faulty determination of the equivalent of silicon. The same difference is detected in several other cases. After tracing these differences, he remarks that this number 44-45 plays an important part in the science of stoichiometry and the relations which depend upon it are supported, in some cases at least, in a remarkable manner, by analogies of atomic volume. These analogies are pointed out in a series of tables. The author concludes that this relation extends to 48 of the known elements, to all whose equivalents are well known except the group O, S, Se, and Te "substances which stand alone and unmistakably apart from the other elements." This same difference 44 is beginning again, in these later days, to attract attention in considerations of the atomic weights. Lea did not make much use of the negative equivalents given by him in his tables, still they were criticized. So in a subsequent paper (40) he met these criticisms by the statement that these numbers with the negative sign were mere mathematical abstractions and of course did not mean "less than nothing." Considered in connection with the operations by which they were produced, they are full of significance.

45. The Geometrical Ratios.—Another paper (45) was devoted to what he called geometrical ratios. He first offered as an explanation of the arithmetical relations, already discussed, the hypothesis that the common difference in a series of elements might represent the equivalent number of a substance, as yet undetermined, which by

its combination in varying proportions gave rise to the successive terms of the series.

He noted that if we take two substances and examine the ratio which subsists between the numbers representing their atomic weights, we may find, in certain cases, that it is identical with the ratio subsisting between the atomic weights of two other substances and so on through a considerable number of elements. The ratio between the atomic weights, for instance, of O and N is that of four to seven, so likewise is that between Zr and K; or K and Ba. He then gave a table in which the elements are arranged according as they give this oxygen-nitrogen ratio of  $\frac{4}{7}$ , and a second table for the carbon-nitrogen or  $\frac{3}{7}$  ratio.

A different mode of expressing these relations is gotten when instead of adopting the equivalent of one element as oxygen or hydrogen as a permanent unit, we successively make those of the left-hand members of the proportion the units, say 100, then of course all the right-hand members will have the equivalent 175, or for the second ratio some different number will be gotten.

46. Other Regularities.—These ratios are traced in sundry ways for many elements. The author did not regard them as having any very evident explanation. He further traced various obscure relationships in the group of the halogens, thus: I = 10 Cl - 12 F;  $Cl = \frac{12 \text{ Br} - 7I}{2}$  etc., etc. A table is also given, beginning with Mg=12, and using oxygen as an increment, and the coincidences with known elements are noted, and

also another table beginning with O=8 and using the same increment. The author very aptly added that it is difficult to fix the exact importance to be attached to the various numerical regularities hitherto observed among the atomic weights, some being mere casual coincidences, and sometimes relations remarkably exact and symmetrical may exist between the atomic weights of bodies which show no analogies in their general properties.

- 47. Physical or Absolute Atoms.—In a last paper (45) the author makes use of the work of Gustav Tchermak, on the subject of the law of volumes of liquid chemical compounds, in which he maintains that many of the substances usually classed as elements, comport themselves as compound bodies and that it is possible to determine from their physical properties the number of "physical" or absolute atoms which he supposes are contained in a chemical atom of such a body. This theory Lea combines with some of the numerical relations formerly noted by him.
- 48. Dumas' Extension of Prout's Hypothesis.—Dumas had taken up and put new life into the hypothesis of Prout in 1840. A little later he had adopted with enthusiasm the suggestion of Marignac that the hypothesis be extended to the half-atom of hydrogen. In 1859 he reiterated his adhesion to the hypothesis and extended it still further to the fourth atom of hydrogen, this having become necessary because of more accurate determinations and the certainty that fractional atomic weights would have to be used for some of the elements. He

found twenty-two atomic weights to be whole multiples of hydrogen; seven atomic weights were multiples of the half atomic weights: and three were multiples of the fourth atom.

Further he found that analogous bodies have identical atomic weights or those with very simple relations between them. And again, the equivalents of elements in the same family furnish laws analogous to those furnished by the numbers representing the equivalents of organic radicals belonging to the same natural series.

He formulated the two following propositions.

- 1. The natural classification of non-metallic bodies is based on the character of the compounds which they form with hydrogen, on the ratio in volumes of the two elements which combine, and in the mode of condensation.
- 2. The natural classification of the metals and in general, of the bodies which do not unite with hydrogen, should be based on the character of the compounds which they form with chlorine, and so far as possible on the ratio in volumes of the two elements which combine and the mode of condensation.
- 49. Criticisms of the Work of Dumas.—Schneider (33) regardep the work of Pettenkofer and Dumas as important steps toward the upbuilding of a natural system. He criticised the propositions of Dumas in detail, differing with him especially as to several elements having the same atomic weight. He pointed out further that the extension of the hypothesis of Prout to the fourth of an atom of hydrogen really deprived it of all

interest and value. The extension could just as well be carried out to the eighth of an atom and so ad infinitum.

Schafarik (38) thought that the observations of Dumas upon the atomic weights opened up brilliant glimpses. He regarded them as the last and clearest expression of a movement of the age. "If the simple bodies group themselves into series as do the organic still many blanks remain to be filled. But when one sees what Gerhardt's series have accomplished for the organic chemist he can not drive out similar expectations for the inorganic. And when once the series of simple radicals are full, we will surely learn to accomplish with them what we can already partially do for the compound radicals—build them up."

50. The Work Accomplished.—From the extracts which have been given, it has been seen that the decade from 1850 to 1860 was one of great activity in the line of discovering all sorts of numerical relations between the atomic weights, a sort of blind groping, feeling that there was an underlying law to be discovered and reaching out after it without avail. It is not strange that many of the relations should have been very fanci-Nor is it wonderful that they failed to see the law at the bottom of these regularities or the explanation of them. The natural law could not be discovered with such incorrect atomic weights as were at their service. Even with our approximately correct weights we are far from seeing the explanation of many of these same relations. The first attempt at arranging the elements in an ascending series according to the magnitude of the atomic weights, was in this decade. This was done by

Gladstone, but failed of any important results, because of errors in the atomic weights. The first diagrammatic representation of the elements, based upon the atomic weights, fell also in this period, Mercer having made the first diagram. Lastly, the analogy to the compound radicals and homologous series was first noted and discussed. Still, one must confess that the brilliant promise of the beginning of the period was far from fulfilled, and it was perfectly natural that chemists generally, should begin to regard the whole subject with indifference or even with ridicule.



## CHAPTER III.

THE IMMEDIATE FORERUNNERS OF THE PERIODIC LAW.

- 51. The New Conditions.—From 1860 on, the way became clearer, and in the succeeding work we catch glimpses of the great natural law until at the close of the decade the law stands fairly stated. At first little attention was paid to the papers containing it, or they were even laughed at, for chemists had become tired of these endless symmetries and regularities offered without explanation and without use. We will see too that occasionally some returned to the same sort of speculations which characterized the sixth decade, oblivious of the changes which had come over the field of work. Two factors enter largely into the improvement in the character of the work of the Chemists were now in the possession of a fairly accurate set of atomic weights and a more extended knowledge of the elements and their compounds. Several elements were added to the list by means of the spectroscope and expectations were aroused that yet others might be discovered.
  - 52. Stas' Opposition to Prout's Hypothesis.—The last serious conflict over this hypothesis took place between Stas and Marignac from 1860 to 1866. In order to test the truth of this hypothesis so earnestly contended for by his old master and co-worker, Dumas, Stas undertook a re-determination of many of the more important atomic weights with a degree of care and accuracy never before attained. The atomic weight of silver was made the central factor in many of these determination.

Stastells us (36) that when he undertook his researches he had "an almost absolute confidence in the correctness of Prout's hypothesis." He had indeed assisted Dumas in his memorable revision of the atomic weight of carbon which had done so much to reinstate this theory. As his newer researches progressed, doubts gradually arouse within him. His results for silver, chlorine, lead, potassium and other elements were clearly not in accord with the hypothesis in its original form and so he was forced to declare against the hypothesis. Marignac (37) reasoned from Stas' own results that Prout's Hypothesis was substantiated rather than disproved. He made use of the two stock arguments of the Proutians; that Stas' numbers were very close approximations to whole numbers and hence could be considered as such, and that those approximations were too numerous to be accidental. This fatal error of rounding off fractions into whole numbers was the very thing which mislead Prout at the beginning and with him there was far more excuse for it. Marignac further said that should future determinations of other elements give similar approximations he would feel assured of the existence of some fundamental cause which brought about the multiple relation of the atomic weights and subordinate causes which modified it. He thought that Prout's Law deserved to rank with that of Gay Lussac or of Mariotte.

In another place (61) Marignac speaks of Prout's Law as one of those not absolute but only approximate laws, like many other Natural Laws, and says in regard to the assumption of a primal matter, or protyle, that its

atomic weight could be taken as small as might be necessary.

It could well be classed then with what Pettenkofer calls "the attractive and misleading simple laws of Nature." The "rounding-off" passion was called by Berzelius most aptly "Multiplen-Fieber."

53. Other Numerical Relations.—The craze for searching out such regularities as has been recorded in the previous chapter seems to have largely subsided. Most of the work from now on shows a marked difference in aim and method. There is mainly a striving after classification, not disjointed triads, nor unconnected families, but a continuous series of some sort. Besides most of the work now before us is tinged more or less with the idea of periodicity. Still there are a few of the old style of numerical relations to be mentioned. They can best be considered together.

In 1864 a short article appeared in the London Chemical News (48) headed "Numerical Relations of Equivalent Numbers" and signed "Studiosus." In this it was noted that the atomic weights of the elementary bodies, with few exceptions, were either exactly or very nearly multiples of eight. This can be compared with the work of Dumas and Pettenkofer of which Studiosus seems ignorant.

Newlands opposed this generalization. The matter was further discussed by Noble (51) who disapproved of using the term "law", as Studiosus had done, for such relations. Some of these he said, were interesting, others were rubbish. Other brief notes on the subject

appeared from "Inquirer" and from "Studiosus", and there the matter rested. The fact that many writing upon these subjects concealed their identity under fictitious names would indicate that confidence had been lost in them and that they were looked upon with disfavor

54. Parallelism Revived.—Several years later (1869) an anonymous paper appeared (68) in the American Supplement to the London Chemical News. This paper considered the parallelism of the elements in a different way from the Double Parallelism of Dumas and in a broader sense, though the ideas do not greatly differ. The diagram given is similar in some respects to some of the diagrammatic representations of the Periodic Law which appeared a number of years afterwards, though it is evident that this unknown author had no idea of the law in making his diagram. The prominent idea with him was the parallelism, or pairing of the elements.

A central vertical line represented the increase in atomic weights and the different elements were placed along it at heights corresponding to their atomic weights and at such distances as to throw those of the same series in columns together.

"The atomic weights seem to arrange themselves on the diagonal, in parallel shelving lines; also there is a correspondence between the series of artiads and perissads which have the highest atomic weights, that is to say, Na, K, Rb, Cs, and Tl on the one hand and Mg, Ca, Sr, Ba, and Pb on the other, inasmuch as they form strong bases and peroxides but no suboxides or acids." And so this parallelism was traced for the two series having the next highest atomic weights &c. Also special resemblances were pointed out between the elements occupying corresponding places in the series as C and F, S and P, Ca and K, &c.

The author then observed that the regularity to be detected is certainly a very rude one but "considering that every different combination of molecular elasticities (as shown by spectral lines) must give a new set of properties and considering that only about sixty elementary substances out of the myriads which might exist are known to us, we ought to expect no more accurate classification of them than could be made of the animal kingdom, if only sixty animals were known."

**55.** The Pairing of the Elements.—A short time before the appearance of the article just discussed, another (69) was published in the same journal, also anonymous, and dealing with a sort of parallelism.

Here, too, a table was given, in which the elements were arranged in two columns according to their even or odd valencies, and at the same time observing the order of their atomic weights. It was claimed that an inspection of the table showed that the elements were brought into "something like a natural relation with one another." "Where the atomic weights agree in the two columns there is a still further agreement between the corresponding elements; the element of even valence is paired or mated with an element of odd valence. Probably for each column there is a progression of properties from the top to the bottom, in the order and in the

proportion of the numbers, and the discovery of such properties is a fair and open problem."

"Also, the column readily breaks up into smaller columns, or groups. The peculiar relation of the artiads and perissads in Group I is very striking. On one side are all the metals of the known alkalies and each is paired with a well-known alkaline earth."

"The standing out unpaired of H, N, P, As, Sb, and Bi, is very noticeable, for these are the only unmated perissads. There are many unmated artiads, and it is noticeable that many of them occur together. It is possible that they may be filled by the discovery of new elements."

The author thought that more alkalies might be looked for.

| Artiads. | Perissads. | Artiads. | Perissads. |
|----------|------------|----------|------------|
| G1 9     | н г        | Co 58.8  |            |
| C 12     | Li 7       | Yt 61.7  |            |
|          | В п        | Cu 63.4  |            |
|          | N 14       | Zn 65.2  |            |
| О 16     | F 19       | In 72    |            |
| Mg 24    | Na 23      |          | As 75      |
| Al 27.   | 4          | Se 79.4  | Br 8o      |
| Si 28    |            | Sr 87.6  | Rb 85.4    |
|          | P 31       | Zr 89.6  |            |
| S 32     | C1 35.5    | Da 93.6  | Cs 94      |
| Ca 40    | K 39.1     | Mo 96    |            |
| Ţi 50    |            | Ru 104.4 | ,          |
| Čr 52.   | 2 V 51.4   | Rh 104.4 |            |
| Mn 55    |            | Pd 106.6 | Ag 108     |
| Fe 56    |            | Cd 112   |            |
| Ni 58.   | 3          | Eb 112.6 |            |
| &c.,     | &c.,       | &c.,     | &c.        |

| THE | SMA | T.T. G | ROUPS. |
|-----|-----|--------|--------|
|     |     |        |        |

|     | I.   |     |
|-----|------|-----|
| Li  |      | G1  |
| Na  |      | Mg  |
| K   |      | Ca  |
| &c. |      | &c. |
|     | II.  |     |
| F   |      | О   |
| C1  |      | S   |
| Br  |      | Se  |
| I   |      | Te  |
|     | III. |     |
| Ag  |      | Pd  |
| Au  |      | Pt  |
| Pb  |      | T1  |
|     | &c.  |     |

- 56. Classification by the Atomicities.—It should be mentioned in this connection that in 1864 Williamson (50) had presented before the Royal Institution a "Classification of the Elements in Relation to their Atomicities." Much credit is due Williamson for assisting in the introduction of Cannizzaro's views concerning the atomic weights among English chemists and in suggesting the same changes in Gerhardt's system, which had been chiefly used up to that time. This put a new and fairly correct table in the hands of chemists.
- 57. Relation between the Atomic Weights and Densities.—A new line of research was struck out by Fleck (58) in 1864 by his work upon the "Relations Between the Chemical Equivalents and the Densities of Bodies." Intimations of some sort of connection between the atomic weights and the properties lie, of

course, in the idea of the triads and in much of the preceding work, but they were not clear. Here we have a distinct search for such relations, though not a very successful one. The day was still some distance off when the dependence of the properties upon the atomic weights would come to be recognized.

Fleck found that the simple bodies, or elements, form several groups in which the relation of the equivalents to the square of the density is invariable, and these constant volumes are generally entire multiples of the value borne to potassium.

58. Brodie's Ideal Chemistry.—This is perhaps the best place to mention the efforts of Brodie (66) to substitute a new chemical theory and system in opposition to the atomic theory. It appeared as a long article of one hundred pages in the Journal of the London Chemical Society, and was discussed and antagonized by many authors, as Jevons, Williamson, Odling, Kekulè, Ward, Crum-Brown, and others.

The paper is a speculative one and is referred to here because of the attention aroused by it, because it is quoted by later authors, and because of its bearing upon that side of the subject of this treatise, which was often adverted to in the earlier speculations and which underlies much of the thought and work upon the Periodic Law, namely, the composite nature of the elements.

Brodie discussed first the inadequacy of the chemical symbols. He suggested as a foundation for a new and more correct principle the unit of each body in a gaseous condition, *viz.*, that unit of gaseous weighable matter

which fills a space of 1000 cc. at 0° and 760 mm. pressure.

This unit of mass, empty, may be designated I. Now let S designate the operation by which the unit of mass is filled with the unit of weight, then S<sup>3</sup>I would mean this unit of mass filled with a stuff of three times the condensation, etc. Such a system of symbols would give at the same time the operation and its result. The symbol of the compound is at the same time the symbol according to which the combination took place. The following may be taken as examples:

| Unit of mass = I | $S = t_2$         |
|------------------|-------------------|
| H = a            | $H_2S = at$       |
| $O = x_2$        |                   |
| $H_2O = ax$      | $SO_3 = tx_3$     |
| $H_2O_2 = ax_2$  | $H_2SO_4 = atx_4$ |

Thus the hypothesis is made that the symbol of hydrogen be a, and hydrogen is formed by one of the abovementioned operations. Then oxygen (x) represents two operations; the same also of water.

This use of symbols, according to Brodie, should give us an insight into the nature of matter. There are, he thinks, different classes of elements.

- 1. Those which were formed by one operation (as H and Hg.)
- 2. Those in whose formation two similar operations were carried out.
- 3. Those which must be designated compound (as Cl out of a, and an unknown element c.) In these compound elements we come across units of unknown ele-

ments, as c, i, n. Whether these exist or not, Brodie does not profess to know. Their unit symbols answer every condition of real existence. Perhaps they were once free upon the earth, but have become indissolubly combined upon its coolings. Brodie says he does not aim at proving the existence of a primal matter, but only to make the existence of these compound elements probable.

It is scarcely necessary to subject such speculations to criticism.

59. Brodie's Conception of the Genesis of the Elements.—With regard to the existence of these elements, out of which our present elements are made up, he says:

"We may conceive that in remote time or in remote space, there did exist formerly, or possibly do now exist, certain simpler forms of matter than we find on the surface of our globe,  $\alpha$ ,  $\chi$ ,  $\varepsilon$ ,  $\nu$ , and so on. We may consider that in remote ages the temperature of matter was much higher than it is now, and that these other things existed then in the state of perfect gases, separate existences, uncombined.

"We may then conceive that the temperature began to fall, and these things to combine with one another and to enter into new forms of existence, appropriate to the circumstances in which they were placed. \* \* \* We may further consider that as the temperature went on falling, certain forms of matter became more permanent and more stable, to the exclusion of other forms.

We may conceive this process of the lowering of the temperature going on, so that these substances, when once formed, could never be decomposed, in fact, that the resolution of these bodies into their component elements could never occur again. You would then have something of our present system of things.

"Now, this is not purely an imagination, for when we look upon the surface of our globe, we have actual evidence of similar changes in Nature. When we look at some of the facts which have been revealed to us by the extraordinary analyses which have been made of the matter of distant worlds and nebulae, by means of the spectroscope, it does not seem incredible to me that there may even be evidence, some day, of the independent existence of such things as x and y."

It is perhaps not so very surprising that such baseless speculations as these should have received more attention and more approval than the Law of Octaves of Newlands. Where boundless space and limitless possibilities are taken into consideration, no proof is possible and none can be required, and such free flights of the imagination are always attractive to certain minds.

60. The Telluric Screw of De Chancourtois.—It is to De Chancourtois, an engineer and geologist, that the credit of being the first to devise a symmetrical arrangement of the elements is generally given. He may in some measure be regarded as the originator of the periodic law, though his work lay unnoticed for thirty years and the periodic law was developed independently

of it. In 1862 (46) he presented to the French Academy of Science a paper on a "Natural Classification of the Simple or Radical Bodies entitled the Telluric Screw (Vis Tellurique)." Several communications followed and it was all finally put in the form of a lithographic table which summed up all his ideas and was accompanied by certain general considerations on the numerical character of the simple bodies, as well as on the verifications which spectral analysis might furnish. In this paper is found the very explicit assertion as "the first general conclusion from his work." "Les propriétés des corps sont les propriétés des nombres." The most important part of the Periodic Law is that the properties of the elements are determined by and are dependent upon the atomic weights. De Chancourtois' statement is obscure but may be looked upon as conveying in part the same idea.

The fundamental idea of the Telluric Screw consisted in writing the values of the atomic weights along the generatrix of a vertical cylinder, the circular base of which was divided into sixteen equal parts, sixteen being the atomic weight of oxygen. If we then trace upon the cylinder a helix with an angle of forty-five degrees to its axis, each point of the helix may be considered as the characteristic point of a simple body, the atomic weight of which, proportional to the corresponding length of the spiral, will be read upon the generatrix which passes by this point. At each turn, the helix returns on one and the same perpendicular at distances from the summit of the cylinder which are multiples of

sixteen, and mark the bodies whose atomic weights conform to this condition.

"In the same manner the various points of intersection of the helix with any of the sixteen principle generatrices, traced from the divisions of the circular base. correspond to elements whose atomic weights differ among themselves by sixteen, or by a multiple of sixteen. Lastly, if after having developed the cylinder upon a plane which transforms the helix into a series of straight parallel segments, we join by a straight line any two points taken upon two segments, after coiling up, this right line will produce a secondary helix, and the intersections of this latter with the various turns of the principal helix will mark bodies for which the differences of the atomic weights will be multiples of a constant quantity. In this manner the Telluric Screw, by simply drawing right lines, enables us to show numerical relations which it would have been less easy to detect by a mere inspection of the numbers."

"The relation of the properties of the bodies are manifested by simple relations of position of their characteristic points: and then, each of the helices carried through two characteristic points and passing by several other points, or merely in their proximity, shows relations of properties of a certain kind, the analogies or the contrasts being manifested by certain numerical orders of succession like the immediate sequence or the alternations at diverse periods."

De Chancourtois thus gives a classification of the elements according to their atomic weights and indicates the idea of periodicity. He says, "We cannot refrain from remarking the predominance of the number 7 in the types of the groups occupying the spiral which are best filled out."

In his pamphlet, published in 1863, he speaks of "direct developments of the system which enable us to perceive at the same time approximations of the series of numerical characteristics to the series of musical sounds, and to that of the bands and rays of the spectrum."

For this résumé of the work of de Chancourtois I am indebted to Lecog de Boisbaudran and A. de Lapperent (198), and Crookes (199). It has been compared with the original. In their critique of the work they say that they are far from pretending that the theory of the screw is free from faults, and that the author had not grafted upon his work many considerations which it would have been better to leave out. Several approximations were inaccurate or were strained, and some of them evince too free a use of the imagination. De Chancourtois started out with the idea that in the natural series the differences between the atomic weights ought to be constant. Gaps were filled up by imagining new varieties of known simple bodies which he called Secondary Characters, and this often led him to mistaken analogies.

61. The Work of Newlands.—A second worker, to whom credit is due as to one who grasped some of the truths of the Periodic Arrangement, was John A. R.

Newlands. His work followed immediately upon that of de Chancourtois, but was quite independent of it. His first paper (47) was devoted to the consideration of some numerical relations between the atomic weights. These relations were in part along the line of the old triads, thus zinc was pointed out as the mean between magnesium and cadmium, copper between cobalt and zinc. In the group of the alkalies, one of lithium and one of potassium made two of sodium; one of lithium and two of potassium made one of rubidium, etc. Similar relations were observed for other groups. He also endeavored to show a certain kind of symmetry when the lowest member of a group was subtracted from the next higher member and when the lowest member of a triad was deducted from the highest. These were not very obvious. In his first work he used the old atomic weights but speedily abandoned them for those of Cannizzaro.

In a second paper (53) he gave a table containing the elements arranged in the order of their atomic weights. In a side column the differences between these weights were given, each being deducted from the one next higher in the scale. He failed to find any regularity in these differences, in fact the table was made to disprove the supposed law of one "Studiosus," who had maintained that the atomic weights of the elementary bodies were, with few exceptions, either exactly or very nearly multiples of eight, and whose work has been already mentioned. This has been claimed as the first arrangement of the elements in the order of their atomic weights, but

was preceded by nearly ten years by the arrangement of Gladstone, in which, however, the atomic weights were so faulty that no regularities were discovered, and it is also antedated by the arrangement of de Chancourtois. The remainder of his paper was devoted to a discussion of some triads and he noted the recurrence of the number sixteen as the difference number between the first and second numbers of some of the best known triads.

62. The Law of Octaves.—It was in a third paper (54), published a month later, that he began to pay attention to the possibilities of his new arrangement of the elements in the order of their atomic weights. In that paper he stated that if these elements are numbered 1, 2, 3, &c., "it will be observed that elements having consecutive numbers frequently either belong to the same group or occupy similar positions in different groups." "The difference between the number of the lowest member of a group and that immediately above it is 7; in other words, the eighth element starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music. The differences between the numbers of the other members of a group are frequently twice as great; thus in the nitrogen group, between N and P there are seven elements; between P and As 13; between As and Sb, 14 and between Sb and Bi, 14."

At the close of the paper, he referred again to his triads, and spoke of the apparent existence of triads where the middle members were unknown and also the possibility of Mn, Fe, Co, Ni, and Cu, being the centres of triads whose extremes were unknown or unrecognized. On

the discovery of indium, he hastened to suggest a place for it among the triads and also in his new system (55).

One year after his first announcement of the new system of the atomic weights in numerical order, Newlands published a paper (56), giving his discovery a name and proclaiming it to be a "law." The paper was entitled "On the Law of Octaves." In the table which he gave, he transposed some of the elements so as to bring them into their proper groups. He observed that elements belonging to the same group "usually" appear on the same horizontal line. He next declared that "all the numerical relations among the equivalents pointed out by M. Dumas and others, including the wellknown triads, are merely arithmetical results flowing from the existence of the Law of Octaves." Pursued by what might well be called, in his case and in many others, a mania for hunting out arithmetical relations, he tried to discover some sort of relationship between the numbers given the elements as they fall in their places in the system and their atomic weights.

63. Explanation of the Existence of Triads.— He offered (57) as an explanation of the existence of triads the fact that, "in conformity with the Law of Octaves, elements belonging to the same group generally have numbers differing by seven or by some multiple of seven. That is to say, if we begin with the lowest member of a group, calling it 1, the succeeding members will have the numbers 8, 15, 22, 29, &c respectively. But 8 is the mean between 1 and 15; 15 is the mean between 8 and 22 &c. and therefore as an arithmetical result of the Law of Octaves

the number of an element is often the exact mean of those of two others belonging to the same group and consequently its equivalent also approximates to the mean of their equivalents."

Newlands' Table of the elements, as given in 1866, is reproduced here.

| ELEMENTS ARRANGED IN OCTAVES. |       |                |              |  |  |  |  |
|-------------------------------|-------|----------------|--------------|--|--|--|--|
| No.                           | No.   | No.            | No.          |  |  |  |  |
| Н 1                           | F 8   | C115           | Co and Ni 22 |  |  |  |  |
| Li 2                          | Na 9  | К16            | Cu23         |  |  |  |  |
| G 3                           | Mg 10 | Ca17           | Zn24         |  |  |  |  |
| Во 4                          | A111  | Cr18           | Y 25         |  |  |  |  |
| C 5                           | Si 12 | Ti19           | In26         |  |  |  |  |
| N 6                           | P13   | Mn20           | As 27        |  |  |  |  |
| O 7                           | S     | Fe21           | Se 28        |  |  |  |  |
| Br29                          | Pd 36 | Te43           | Pt and Ir50  |  |  |  |  |
| Rb30                          | Ag 37 | Cs44           | Os51         |  |  |  |  |
| Sr31                          | Cd 38 | Ba and V···45  | Hg 52        |  |  |  |  |
| Ce and La. 32                 | U 39  | Ta46           | T153         |  |  |  |  |
| Zr33                          | Sn40  | W · · · · · 47 | Pb54         |  |  |  |  |
| Di and Mo 34                  | Sb41  | Nb48           | Bi 55        |  |  |  |  |
| Ro and Ru . 35                | I 42  | Au49           | Th 56        |  |  |  |  |

In order to allow for certain elements which have their atomic weights very close together, as cobalt and nickel, Newlands modified his law thus; "The numbers of analogous elements, when not consecutive, differ by seven, or by some multiple of seven."

## ORDRE DE RECUR-RENCE DANS SPIRES NOMBRES PREMIERS NOMBRES COMPLEX PARLENS COMPLEX PARLENS FACTOUS TABLEAU NOMBRES NATURELS DES CARACTERS GEOMETRIQUE (DEVELOPPEMENT D'UN CYLINDRE DE 0,025 DIAMETRE) 012345678910111213141516 23 216 8 23 25/10 1 19 2

22346 47 47 64. Criticisms of Newlands' Law.—Dr. Gladstone objected to the arrangement on the score of no room being left for elements which might still be discovered. Further there seemed to be about as close an analogy between the elements in the last vertical column as between those in any horizontal line. Professor G. F. Foster condemned the arrangement because of the distance placed between manganese and chromium or iron and cobalt and nickel.

In reply to the criticism of Gladstone, Newlands said that the fact that such a simple relation existed now was presumptive proof that it would continue to exist no matter how many elements should be discovered. The difference in the numbers of the analogous elements might be altered to eight or any conceivable number without destroying the simple relation between the numbers of analogous elements.

Very little attention was paid to this work of Newlands. In fact it was allowed to drop completely out of sight as was the somewhat similar work of De Chancourtois. It was not brought to light again until after the system of Mendeléeff had become famous.

65. Character of the work of De Chancourtois and Newlands.—With regard to the work of these two, De Chancourtois and Newlands, it is certain they recognized the fact that periods of seven existed. They failed to extend the idea fully to properties other than the atomic weights. The arrangement of the elements in the order of their atomic weights had been tried a number of years before

the papers of these two workers appeared. De Chancourtois seems to have had some glimpse of the dependence of the properties upon the atomic weights. These two investigators then really cover many of the important points of the Periodic Law. Their failure to impress their views upon their contemporaries came from a lack of clearness of statement, from faulty atomic weights and arrangement, and from their complicating matters and obscuring the truth by useless and false speculations.

Mendeléeff (181) has criticised their work as follows: "In such attempts at arrangement and in such views are to be recognized the real forerunners of the Periodic Law; the ground was prepared for it between 1860 and 1876, and that it was not expressed in a determinate form before the end of the decade, may I suppose, be ascribed to the fact that only analogous elements had been compared (vid. M. Carey Lea). The idea of seeking for a relation between the atomic weight of all the elements was foreign to the ideas then current, so that neither the Vis Tellurique of De Chancourtois, nor the Law of Octaves of Newlands, could secure anybody's attention. And yet both De Chancourtois and Newlands, like Dumas and Strecker, more than Lennsen and Pettenkofer, had made an approach to the Periodic Law and had discovered its germs.

"The solution of the problem advanced but slowly, because the facts, and not the law, stood foremost in all attempts; and the law could not awaken a general interest so long as elements, having no apparent connection with each other, were included in the same octave."

66. Remarks of Crookes upon the Priority Claims.— With regard to the claim of priority advanced for De Chancourtois and Newlands Crookes says (199) "The Periodic Law, it must be remembered, when first announced was not immediately accepted. When Mr. Newlands read his memoir before the Chemical Society it by no means met with a very enthusiastic reception. One gentleman present even inquired, sarcastically, whether the author had ever arranged the elements according to the order of their initial letters.

"Then came the announcements by Professors Mendeléeff and L. Meyer of their independent and simultaneous discovery of the same truth. The details were quickly circulated and discussed in the scientific press, and the respective merits of the two savants was for a time a bone of contention. Professor Mendeléeff said: It is possible that Newlands has prior to me, enunciated something similar to the Periodic Law, but even this cannot be said of L. Meyer.

When the successful attempt was made to vindicate the claims of Newlands as the first discoverer, the question was thoroughly rediscussed. But none of the savants who entered into the question ever breathed the name of De Chancourtois. His memoirs were at all times accessible in the *Comptes Rendus*. But no one found in them that meaning which M. de Boisbaudran and de Lapperent now assert. They certainly contain a proposal to classify the elements with reference to their atomic weights. But we may be permitted to doubt

whether they can be fairly considered as the germ of the Periodic Law.

"In going over old researches we often find in them matter which we may now regard as a forecast of subsequent discoveries; but there is no sufficient evidence that the author disentangled such matter from accompanying speculations. In the memoir (of de Boisbaudran and de Lapperent) we find an admission that such has been the case with the writings of M. De Chancourtois."

67. The First Table of Lothar Meyer.—In the year 1864, that is, two years before the presentation of Newlands'paper before the Chemical Society of London, containing his Law of Octaves, but about the time of his first publication, Lothar Meyer published the first edition of his "Modern Theories of Chemistry" (59) and in it gave a table of the elements arranged horizontally according to their atomic weights, so that analogous elements stood under one another and the change of valence, along with that of atomic weight, could be easily observed. Besides, the difference numbers between these weights, taken horizontally, were also given. Some elements were not included in the list and others were given inaccurately, thus impairing the value of the table. The second, third and fourth series are given here as illustrations.

|         | IV.     | III.    | II. I.           | I.       | II.     |
|---------|---------|---------|------------------|----------|---------|
| 2. Ser. | C 12.0  | N 14.04 | O 16.0 F 19.0    | Na 23.05 | Mg 24.0 |
| Diff.   | 16.5    | 16.96   | 16.07 16.46      | 16.08    | 16.0    |
| 3. Ser. | Si 28.5 | P 31.0  | S 32.07 C135.46  | K 39.13  | Ca 40.0 |
| Diff.   | 44.45   | 44.00   | 46.70 44.51      | 46.30    | 47.6    |
| 4. Ser. |         | As 75.0 | Se 78.8 Br 79.97 | Rb85.40  | Sr 87.6 |
|         | 44.45   | 45.60   | 49.50 46.80      | 47.60    | 40.5    |

It is clear from the part of the table given that the idea of the natural families, already well known, was the predominant one, and that the numerical order of the atomic weights was subordinated to it. Thus the four first elements form a series and then the others are in sixes. Some elements are omitted and vacant spaces are left in other cases. In the fourth series, we have the first member omitted in order that analogous elements may fall properly. No places were found in the table for copper, silver and gold, and other elements. There is certainly less evidence of periodicity in this arrangement than in the preceding one of Newlands and vet underlying the system, though probably unrecognized or unappreciated by even the author at the time of its publication, are the two great principles of the ascending series of atomic weights and the stated recurrence of elements with similar properties. It was Mever's first attempt, imperfect and incomplete, but sufficient to start that brilliant thinker along the right road and lead him ultimately to the great discovery. The complete table of 1864 will be given later on.

68. Hinrichs' Deductions from the Spectra of the Elements.—Following up his hypothesis of one primary form of matter, first announced twelve years before, Hinrichs called the recent developments in spectroscopy to his aid in the investigation. Making use of the Plucker and Ditscheiner's determinations of the wave lengths in various spectra of the metals, he drew the following conclusions (from thirteen elements considered).

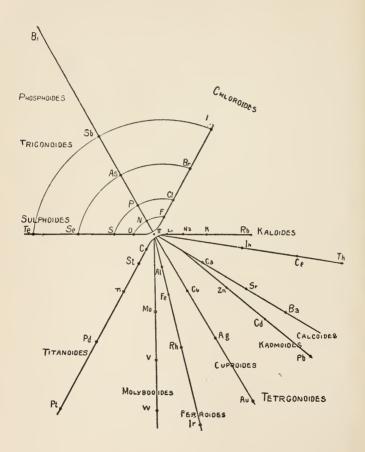
"The dark lines of the elements are equidistant throughout the spectrum, but of varying intensity, many not being observed (or observable) at all; the intervals between the observable lines are expressible as simple multiples of the equal distance indicated by all."

Further, by considering the spectra of seven elements, he found that the "dark lines of the elements are related to the atomic dimensions, considering the elements composed of one single primary element, Urstoff."

He concluded by promising a series of articles which should show that, "the properties of the chemical elements are functions of their atomic weights," and that, "the unity of matter is as real as the unity of force."

These are indeed remarkable statements, coming as they do three years before Mendeléeff announced, in his Periodic Law the dependence of the properties upon the atomic weights, and almost in the same language.

69. The Pantogen of Hinrichs.—This theory, Hinrichs states, was first communicated to various learned men and academies of Europe in 1856 and 1857. It may be stated, beforehand, that Hinrichs is a believer in the Proutian Hypothesis as extended by Marchand and Dumas. This pantogen is the constituent of the various elements. Atoms of pautogen he called "pan atoms." It is necessary to consider them as material points, without any hidden occult property. When combined, these atoms (all equal) are at definite distances. Those of three atoms form a regular triangle. Chemical elements whose atoms are made up of such figures are called Trigonoides



(corresponding to non-metals.) Four panatoms form a square and elements whose atoms are composed of such figures are called Tetragonoides (metals). Elements are thus classified according to the form of their atoms. The Trigonoides and Tetragonoides form the true orders of the elements. These orders are divided into families and the families into species or elements. The families can be expressed by an algebraic equation. Thus the "phosphoides" will be Ph = m (p). These are the elements N, P, As, Sb, Bi. In the equations given, p is a regular hexagon. For the halogens, or as they are called by the author, "chloroides," the equation is Ch = (I)+m. p where m=5.

In the organic series (homologous) he saw the prototypes of the elements.

His chart of the elements is here reproduced. The radii in this mark the genera and the spiral cutting them, according to the order number, marks the elements, the distance of the species from the centre being proportional to its atomic weight.  $\pi$  as the symbol of pantogen, is placed at the centre of the chart.

It is evident from this citation from Hinrich's Program der Atomechanik that it bears little relation to the Periodic Law. The author states in a later publication that it contains, explicitly stated, all that is true in the Periodic Law. He is a vigorous critic and opponent of this law, however, and may mean by this statement that he regards very little of it as true. The leading facts of his system seem to be drawn from of the Proutian Hypothesis of the composite nature of the elements and the

old well-recognized families, falling in the two imperfect divisions of non-metals and metals.

The diagram which he gave is undoubtedly the precursor of the spiral arrangement of Baumhauer and others, although the fundamental ideas are not identical.



## CHAPTER IV.

THE ANNOUNCEMENT OF THE PERIODIC LAW. 1869-1871.

- 70. Periodic Law.—We come now to the period of the announcement of the Periodic Law. The numerical relations already given form an important part of the Natural Law which one may believe will in time be recognized as something higher and broader than what is now known as the Periodic Law. Some of these regularities are doubtless fanciful, the importance of others is not yet fully understood and all are too often overlooked in the prominence ascribed to the ascending series of atomic weights and their regular periodicity. Much credit is due to the early investigators who worked over the strange coincidences and connections between these important physical constants.
- 71. Mendeleeff's First Paper.—The first paper summing up all the more important principles of the Periodic Law was one laid by Mendeléeff before the Russian Chemical Society in March 1869. (70.) The conclusions reached in that paper were as follows:
- 1. The elements, if arranged according to their atomic weights, exhibit an evident periodicity of properties.
- 2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (e.g., platinum, iridium, osmium) or which increase regularly (e.g., potassium, rubidium, cæsium).
- 3. The arrangement of the elements, or groups of elements, in the order of their atomic weights corresponds

to their so-called valences as well as, to some extent, to their distinctive chemical properties—as is apparent, among other series, in that of lithium, beryllium, barium, carbon, nitrogen, oxygen and iron.

- 4. The elements which are most widely diffused have small atomic weights.
- 5. The magnitude of the atomic weight determines the character of the element just as the magnitude of the molecule determines the character of a compound body.
- 6. We must expect the discovery of many yet unknown elements, for example, elements analogous to aluminium and silicon, whose atomic weight would be between 65 and 75.
- 7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.
- 8. Certain characteristic properties of the elements can be foretold from their atomic weights.
- "The aim of this communication will be fully attained if I succeed in drawing the attention of investigators to those relations which exist between the atomic weights of dissimilar elements which, as far as I know, have hitherto been almost completely neglected. I believe that the solution of some of the most important problems of our science lies in researches of this kind."

The chief trouble about this first paper of Mendeléeff lay in the imperfections of his table, which is here given in full. The arrangement was only partially according to the size of the atomic weights. They were arranged in vertical series and some of the atomic weights were incorrect.

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MENDELÉEFF'S TABLE.
                                         1869.
                              Ti
                                    50
                                         Zr
                                               90
                                                     ?
                                                         180
                                                    Ta
                                                         182
                              V
                                         Nb
                                               94
                                    51
                                                    W
                                                         186
                              Cr
                                         Mo
                                               96
                                    52
                              Mn
                                         Rh
                                              104.4
                                                    Pt
                                                         197:4
                                    55
                              Fe
                                    56
                                        Ru
                                              104.4
                                                    Ir
                                                         198
                            Ni.Co
                                    59
                                         Pd
                                              106.6
                                                    Os
                                                         199
H
    1
                              Cu
                                  63.4
                                        Ag
                                              108
                                                    Hg
                                                         200
        Be
                   Mg
                              Zn
                                   65.2
                                        Cd
                                              112
              9.4
                         24
        В
                   A1
                               ?
                                   68
                                        Ur
                                              116
                                                    Au
              11
                         27.4
                                                         197
        C
                               ?
                                        Sn
                    Si
                         28
                                              118
              12
                                   70
        N
              14
                   P
                         31
                              As
                                   75
                                        Sb
                                              122
                                                    Bi
                                                         210
        O
              16
                   S
                        32
                                        Te
                                              128?
                              Se
                                   79.4
        F
              19
                   C1
                                        Ι
                                              127
                        35.5
                              Br
                                  80
        Na
                                  85.4
                                                     T1
              23
                    K
                              Rb
                                        Cs
                                               133
                                                         204
                        39
                              Sr
                                  87.6
                    Ca
                                        Ba
                                                     Pb
                         40
                                               137
                                                         207
                    ?
                         45
                              Ce
                                  92
                              La
                   ?Er
                         56
                                   94
                   ?Y
                         60
                              Di
                                   95
                   ?In
                        75.6
                              Th
                                  118
```

72. Mendeleeff's Horizontal Table.—Mendeléeff used other arrangements of the elements in this first paper, one of which has been generally accepted as the most convenient mode of expressing the Periodic Law, though the vertical rows are placed horizontally and the horizontal series then become vertical.

| Li | Na | K   | Cu  | Rb | Ag | Ca  |    | <b>T</b> 1 |
|----|----|-----|-----|----|----|-----|----|------------|
|    |    |     |     |    | Cd |     |    |            |
| В  | AÎ | • • | • • |    | Ur | • • |    | Bi         |
| C  | Si | Ti  | • • | Zr | Sn | ••  | •• |            |
| N  | P  | V   | As  | Nb | Sb | • • | Тa | • •        |
| O  | S  | • • | Se  |    | Te | • • | W  |            |
| F  | C1 |     | Br  |    | I  |     |    |            |

73. Important Features of the System.—Mendeléeff also brought out the idea that all the elements can be arranged in one single unbroken series made up of consecutive periods. He said "The system can be arranged in the form of a spiral and in this the resemblances principally appear among the members of every other series."

He especially emphasized the idea of periodicity. He said afterwards (117): "The repetition of the word periodicity shows that from the very beginning I held this to be the fundamental property of my system of the elements."

In his paper upon atomic volumes a few months later, (71) he said that his system expressed not only the chemical relationship of the elements but also corresponded with the division into metals and non-metals, made a distinction between the valences, brought together similar elements of different groups, explained the resemblance of the series of the elements to the homologous groups, set aside hydrogen as a typical element, placed near together those elements which are most widely distributed in nature and which accompany each other, showed the faultiness of Prout's hypothesis, and pointed out the relations between the elements conformable to their reciprocal affinities. Lastly he pointed out the relations existing between the specific gravities and specific volumes of the different series of elements, arranged by this system.

74. Mendeleeff's Claim as a Discoverer.—As to his claims as a discoverer, Mendeléeff says later, very truly, that no natural law is discovered all at once. Many

might claim share in the discovery as bringing their contributions of fact orthought, but he is rightly to be regarded as the discoverer or creator, who has discerned not only the philosophical side but also the real, and who has known how to throw such light upon the matter that every one can convince himself of its truth.

He stated that the earlier works upon the numerical relations of the atomic weights were known to him, excepting those of De Chancourtois and Newlands, and that he was principally indebted to Lennsen and Dumas. "I have studied their researches and they aroused me to seek for a true law." (117.)

In the elaboration of his law he counted Carnelley as the only one who had added anything new to it, referring to Carnelley's work upon the melting points and magnetic properties. In this statement he considered only that which had been done up to 1880. As to Lothar Meyer, he denied to him any part in the discovery of this law, conceding only that his graphic representation had made certain properties somewhat clearer.

75. The Reception Accorded the Discovery.—It was in March of 1869 that Mendeléeff announced his law to the Russian Society. In August he presented before the Russian Association of Naturalists a paper upon the bearing of his law upon the volumes of simple bodies. In November a further paper appeared from him extending the application of the new system.

Richter, in a letter from St. Petersburg, October 17, 1869, (77) mentioned Mendeléeff's presentation of his system before the Russian Chemical Society and added: "Ich

glaube dass diese interessanten Formulirung nicht verfehlen werden, Ihre Aufmerksamkeit zu erregen." While it is perfectly true that this and the publication of Meyer, to be mentioned next, did attract attention, the notice given them was not at all in accordance with the greatness of the discovery. It is evident that their importance was not recognized and, it may be added, is not fully realized even yet. So far as can be judged at present, the lecture of Dumas at Ipswich created a much greater stir among chemists, was discussed more and led more immediately to others undertaking work along the same or similar lines

76. The Evolution of Meyer's Table.—The discussion between Mendeléeff and Meyer as to the relative merits of their claims to the authorship of the Periodic Law is one of long standing and has been somewhat hotly waged by the principals and by their supporters.

Meyer's claims are based upon his table, published in 1864 and already given. Further, something less than a year after Mendeléeff, he devised a system of the elements which contained the principal features of the Periodic Law. This system will be discussed a little later on. Meyer stated that it was an expansion of his earlier table and was worked out in entire ignorance of the similar work of Mendeléeff which had appeared in the Russian language some months previously. Before his article was published, however, he saw an abstract of Mendeléeff's article in the *Zeitschrift für Chemie* (N. F. Bd. V. 405.) Such being the state of the case, Meyer claims credit only for points in which he believed he had

improved upon the table of Mendeleeff, or differed from it. In his original article he said that his table was essentially identical with the one given by Mendeleeff.

77. Meyer's Table of 1864.—For purposes of comparison Meyer's first table is here given in its complete form. It will be observed that there are two portions. One of twenty-eight elements in six vertical rows and a second of sixteen in five rows. There is a manifest struggle between the desire to arrange the elements according to the atomic weights and at the same time to have them fall according to their analogies in families. It is well to note the significance attached to the difference-numbers, a signifiance not yet understood nor appreciated.

|   | MEYER                 | r's First           | TABLE.                | 1864.                       |          |
|---|-----------------------|---------------------|-----------------------|-----------------------------|----------|
| 4 va1.  | 3 val.                | 2 va1.              | ı val.                | ı val.                      | 2 val.   |
|   |                       |                     |                       | Li 7.03                     | (Be 9.3) |
| Diff  |                       |                     |                       | 16.02                       | (14.7)   |
| C 12.0  | N 14.4                | O 16.00             | F 19.0                | Na 23.5                     | Mg 24.0  |
| Diff. 16.5                                    | 16.96                 | 16.07               | 16.46                 | 16.08                       | 16.0     |
| Si 28.5                                       | P 31.0                | \$ 32.0             | C1 35.46              | K 39.13                     | Ca 40.0  |
| Diff. 89.1 44.45                              | 44.0                  | 46.7                | 44.51                 | 46.3                        | 47.0     |
| ••••  | As 75.0               | Se 78.8             | Br 79.97              |                             |          |
| Diff. $\frac{89}{2}$ 44.55                    | 45.6                  | 49.5                | 46.8                  | 47.6                        |          |
| Sn 117.6                                      |                       |                     |                       | Cs 133.0                    |          |
| Diff. 89.4 44.7                               | 87.4 43·7             |                     |                       | 35.5                        |          |
| Pb 207.0                                      | Bi 208.0              |                     |                       | (T1 204.0?)                 | Ba 137.1 |
| 4 val.  | 4 val.                | 4 val.              | 2 val.                | ı val.                      | 0,       |
| { Mn 55.1<br>Fe 56.0                          | Ni 58.7               | Co 58.7             | Zn 65.0               | Cu 63.5                     |          |
| ₹ Fe 56.0                                     |                       |                     |                       |                             |          |
| (49.2   |                       |                     |                       |                             |          |
| $Diff \begin{cases} 49.2 \\ 48.3 \end{cases}$ | 45.6                  | 47.3                | 46.9                  | 44•4                        |          |
|   |                       |                     |                       |                             |          |
| Ru 104.3                                      |                       |                     |                       |                             |          |
| Diff. $\frac{92-8}{2}$ 46.0                   | $\frac{92.8}{2}$ 46.4 | $\frac{93}{2}$ 46.5 | $\frac{88.3}{2}$ 44.5 | $\frac{88 \cdot 2}{2}$ 44.4 |          |
| Pt 197.1                                      | Ir 197.1              | Os 199.01           | Hg 200.2              | Au 196.7                    |          |

78. Meyer's Table of 1868.—Lately Seubert, the pupil and friend of Meyer, has published an account (239) of a paper which has come to light since the death of its distinguished author and which shows the independence of Meyer in his work. This was a preliminary suggestion of his System, an elaboration of his work of 1864, written out and handed to his friend and successor in the chair of chemistry at Eberswald, Professor A. Remele, in July 1868. Meyer first learned of its preservation when Remele showed it to him in 1893 after his lecture before the German Chemical Society upon the Periodic Law. He then expressed regret that he had not published it in 1868, even though incomplete. This table is fuller and shows many differences from the earlier one. Fifty-two elements are given and in fifteen vertical rows. There are many imperfections in it. Thus there is no place for boron in it and aluminium is put down twice because of evident doubt as to its proper Even then its proper place is missed. Imperfectly known atomic weights also cause some trouble in the arrangement. Every one must admit that there is a wide step between this table and the one given by Meyer after the publication of Mendeléeff.

|   | SUGGESTION FOR A SYSTEM OF ELEMENTS BY LOTHAR MEYER. SUMMER 1868. |
|---|---|
|   | FOR   |
| ı | Þ   |
|   | SYSTEM  |
|   | OF  |
|   | HLEMENTS  |
|   | вγ  |
|   | LOTHAR  |
|   | MEYER.  |
|   | SUMMER  |
|   | 1868.   |
|   |   |

| N=14.4<br>16.96<br>P=31.0<br>44.0<br>As=75.0<br>45.6<br>Sb=120.6<br>87.4=2.43.7<br>Bi=208.0 | 9             | Cr=52.6   | 1              |
|---|---------------|---|----------------|
| 0=16.00<br>16.07<br>\$=32.07<br>46.7<br>\$e=78.8<br>49.5<br>Te=128.3                        | 10 .          | Mn=55.1<br>49.2<br>Ru=104.3<br>92.8=2.46.4<br>Pt=197.1                          | ы              |
| F=19.0<br>16.46<br>Cl=35.46<br>44.5<br>Br=79.9<br>46.8<br>I=126.8                           | II            | A1=27.3<br>29.7=14.8<br>Fe=56.0<br>48.9<br>Rh=103.4<br>92.8=2.46.4<br>IT=197.1  | <sub>ن</sub> ي |
| Na=23.05<br>K=39.13<br>46.3<br>46.3<br>45.4<br>47.6<br>CS=133.0<br>71=2.35.5<br>Te=204.0    | 12<br>Li=7.03 | A1.=27.3<br>Co=58.7<br>47.8<br>Pd=106.0<br>93==2.465<br>Os=199.                 | 4              |
| Mg=24.0<br>16.0<br>Ca=40.0<br>47.6<br>Sr=87.6<br>49.5<br>Ba=137.1                           | 13<br>Be=9.3  | Ni=58.7   | Cı             |
| Ti=48 42.0 Zr=90.0 47.6 Ta=137.6  | . 14          | Cu=63.5<br>44.4<br>Ag=107.9<br>88.8=2.44.4<br>Au=196.7                          | 6              |
| Mo.=92.0<br>45.0<br>Vd=137.0<br>47.0<br>W=184.0   | 15            | Zn=65.0<br>46.9<br>Cd=111.9<br>88.3=2.44.5<br>Hg=200.2                          | 7              |
|   |               | C=12.00<br>Si=28.5<br>8½-44.5<br>8½-44.5<br>Sn=117.6<br>89.4=2.41.7<br>Pb=207.0 | ∞ .            |

79. Meyer's Table of 1870.—Lothar Meyer's article upon the "Nature of the Elements as Functions of their Atomic Weights" (81) appeared in the year 1870, although written, as he says, in December 1869. table there given is an expansion (116) of his table published in 1864. It is distinguished from it in that the consecutive atomic weights are not arranged horizontally but vertically as in one of the tables of Mendeléeff. He had tried to arrange all the elements in that first table but had been quable to do so because of the numerous erroneous atomic weights. When these were corrected he saw the possibility of arranging all of the elements into one table in accordance with the size of the atomic weights. Although Mendeléeff did say that the weights might be ordered in one single spiral. he did not do this and could not have attached much importance to such an arrangement. In fact it was not possible to so arrange them with the series as first given by him and with the false atomic weights included in Meyer observed, (116) "had Mendehis table. leeff then attached any importance to the formation of a single series he would have, without doubt, chosen other values for these elements. Mendeléeff did not hesitate to "correct" the value of the atomic weights by his table and to insert unknown ones when necessary." A close examination of Mendeléeff's first table will show a struggle between a desire to have a single series according to atomic weights and still to get the analogous elements to fall into periods. The regular recurrence of the periods is brought out better by Newlands in his

scheme though Newlands had more inaccuracies of atomic weights to contend with and less knowledge of the analogies between the elements. Meyer's table is much clearer than that of Mendeléeff and brings out the series of analogous elements better. It is given on page 102.

One claim made by Meyer for this table, is the discovery of what he called double periodicity. This is shown in the table where we see that elements of analogous properties recur in every other column and not in the immediately adjacent ones, thus giving two series of analogous bodies. As has been already shown by the quotation from Mendeléeff's first article the two recognized that the analogy was apparent principally between the members of every other series. These he distinguished later as the "matched and unmatched" series.

80. Mendeleeff's Table of 1871.—Mendeléeff's table given in 1871 (74) was a great improvement over his first. He gave in fact two tables, one giving the horizontal and the other the vertical mode of arrangement. These tables follow on pages 103 and 104.

| IX   | T1=202.7 Pb=206.4 Bi=207.5  |
|------|---|
| VIII | Ta=182.2<br>W=183.5<br>Os=198.6?<br>Ir=196.7<br>Au=196.2<br>Hg=199.8  |
| VII  | In=113.4<br>Sn=117.8<br>Sb=122.1<br>Te=128?<br>I=126.5<br>Cs=132.7<br>Ba=136.8  |
| VI   | Zr=89.7<br>Nb=93.7<br>Mo=95.6<br>Ru=103.5<br>Rh=104.1<br>Pd=106.2<br>Ag=107.66<br>Cd=111.6                                      |
| Δ    | As=74.9<br>Se=78.0<br>Br=79.75<br>Rb=85.2<br>Sr=87.0  |
| ΛI   | Ti=48.0<br>V=51.2<br>Cr=52.4<br>Mn=54.8<br>Fe=55.9<br>Ni=58.6<br>Cu=63.3<br>Zn=64.9   |
| III  |   |
| 11   | B=11.0 Al=27.3<br>C=11.97 Si=28.0<br>N=14.01 P=30.9<br>O=15.96 S=31.98<br>F=19.1 Cl=35.38<br>Na=22.99 K=39.0<br>Mg=23.9 Ca=39.9 |
| I    | Li=7.01   |

## MENDELÉEFF'S TABLE I.—1871.

| II                | Io                          | 9   | 8   | 7                        | 6              | 5  | 4  | 3   | 2   | I  | Series.  |
|-------------------|-----------------------------|---|---|--------------------------|----------------|--|--|---|---|--|--|
| ( <b>Au</b> =199) | :                           | :   |   |                          |                | (Cu=63)  |  | Na=23   |   | H=1  | GROUP I.   |
| Hg=200            | :                           | :   |   | Cd=112                   |                | <b>Zn=</b> 65  | <b>Ca</b> =40  |   |   |  | GROUP II. GROUP III.   |
|                   |                             | <u>:</u>  | ? <b>Di</b> =138  | ln=113                   |                | -=68   | -=44   | A1=27.3   |   |  | GROUP III.<br>R <sub>2</sub> O <sub>3</sub> .  |
|                   |                             | :   | ? Ce=140  | Sn=118                   |                | -=72   | Ti=48  | Si=28   |   |  | GROUP IV.<br>RH4.<br>RO2.  |
|                   |                             | :   | :   |                          | Nb=94          | As=75  |  |   | N=14  |  | GROUP V.<br>RH3.<br>R <sub>2</sub> O <sub>5</sub> .  |
| :                 |                             | i   | :   |                          | <b>Mo</b> =96  |  |  |   | 0=16  | 1  | GROUP VI. GROUP VII. RH2. RO3. R207.   |
|                   |                             | :   |   | <b>I</b> =127            | 001==          |  | Mn=55  | CI=35.5   | F=19  |  | GROUP VII. RH. $R_2O_7$ .  |
| FC-190, Au-199    | 0s=195, In=197              | :   |   | Pu 100, A8=100           | Ru=194, Rh=104 |  | Fe=56, Ce=59   |   |   |  | GROUP VIII.  |
|                   | Hg=200 Tl=204 Pb=207 Bi=208 | ? $Er = 178$ ? $La = 180$ $Ta = 182$ $W = 184$ $Au = 199$ $Hg = 200$ $T1 = 204$ $Pb = 207$ $Bi = 208$ | ? Er=178 ? La=180 Ta=182 W=184 O. Hg=200 Ti=204 Pb=207 Bi=208 | Pa=137   Pi=138   Ce=140 | Cd=112         | ST=87   Y=88   ZT=90   Nb=94   Mo=96   -=100   R     G=108   Cd=112   In=113   Sn=118   Sb=122   Te=125   I=127     133   Ba=137   Pl=138   Ce=140                           Pb=207   Bi=208         Other states of the sta | Cu=63)         Zn=65         -=68         -=72         As=75         Se=78         Br=80           =85         Sr=87         ? Y=88         Zr=90         Nb=94         Mo=96         -=100         R           eg=108)         Cd=112         ln=113         Sn=118         Sb=122         Te=125         l=127           e133         Ba=137         ? Di=138         ? Ce=140               e133          ? Er=178         ? La=180         Ta=182         W=184             e199         Hg=200         Tl=204         Pb=207         Bi=208 | Cu=63)         Ca=40        =44         Ti=48         V=51         Cr=52         Mn=35         Face=78           Cu=63)         Zn=65        =68        =72         As=75         Se=78         Br=80           =85         Sr=87         ? Y=88         Zr=90         Nb=94         Mo=96        =100         R           (g=108)         Cd=112         ln=113         Sn=118         Sb=122         Te=125         l=127           1133         Ba=137         ? Di=138         ? Ce=140                 ? Er=178         ? La=180         Ta=182         W=184             u=199)         Hg=200         Tl=204         Pb=207         Bi=208 | Na=23         Mg=24         AI=27.3         SI=28         P=31         S=32         CI=35.5           39         Ca=40         -=44         Ti=48         V=51         Cr=52         Mn=55         F           Cu=63)         Zn=65         -=68         -=72         As=75         Se=78         Br=80           e-85         Sr=87         ?Y=88         Zr=90         Nb=94         M0=96         -=100         R           g=108)         Cd=112         In=113         Sn=118         Sb=122         Te=125         I=127           1133         Ba=137         ?Di=138         ? Ce=140                ?Er=178         ?La=180         Ta=182         W=184          00 | Na=23   Mg=24   Al=27.3   Si=28   P=31   S=32   Cl=35.5     99 | H=I       H=I       C=12       N=14       O=16       F=19         Na=23       Mg=24       Al=27.3       Si=28       P=31       S=32       Cl=35.5         39       Ca=40       -=44       Ti=48       V=51       Cr=52       Mn=55       F         Cu=63)       Zn=65       -=68       -=72       As=75       Se=78       Br=80         -85       Sr=87       ?Y=88       Zr=90       Nb=94       Mo=96       -=100       R         -92       As=137       ?Di=138       ? Ce=140              -133       Ba=137       ?Di=138       ? Ce=140              -133       Ba=137       ?Di=138       ? Ce=140               -133       Ba=137       ?Di=138       ? Ce=140 |

## MENDELÉEFF'S TABLE II.

| Gr. Ser. 1. | 2.      | 4.      | 6.      | 8.      | IO.     | 12.     |
|-------------|---------|---------|---------|---------|---------|---------|
| I.          | Li 7    | K 39    | Rb 85   | Cs 133  | 10      |         |
| II          | Be 9.2  | Ca 40   | Sr 87   | Ba 137  |         | • • • • |
| III.        | B 11    | ? Se    | Yt 89?  | Di 139? | Er 175? |         |
| IV.         | C 12    | Ti 48   | Zr 90   | Ce 141  | La 180? | Th 231  |
| V.          | N 14    | V 51    | Nb 94   | ? 2     | Ta 182  |         |
| VI.         | O 16    | Cr 52.5 | Mo 96   | ?       | W 184   | Ur 240  |
| VII.        | F 19    | Mn 55   | • • • • |         | • • • • | • • • • |
| VIII        |         | Fe 56   | Ru 103  | • •     | Os 194  |         |
|             |         | Co 58.6 | Rh 104  | • •     | Ir 195  |         |
|             |         | Ni 58.6 | Pd 106  | • •     | Pt 197  | • • • • |
| I. HI       | Na 23   | Cu 63.5 | Ag 108  |         | Au 197  | ••••    |
| II.         | Mg 24   | Zn 65   | Cd 112  | 3       | Hg 200  |         |
| III.        | Al 27.3 | Ga 69   | In 113  | • •     | Tl 204  |         |
| IV.         | Si 28   | ???     | Sn 118  | • •     | Pb 204  |         |
| V.          | P 31    | As 75   | Sb 120  | • •     | Bi 208  | • • • • |
| VI.         | S 32    | Se 79   | Te 125? |         |         |         |
| VII.        | C1 35.5 | Br 80   | I 127   | • •     | • • • • | • • • • |

In a foot note it was stated that possibly Di had an atomic weight of 146 and would occupy place marked 2. In another note he spoke of Carnelley's having assigned Norwegium to place 3. These tables contain the Periodic Law as it is known to us. They have not been very materially altered, though they have been corrected in minor points. The work since has been mainly one of elaboration. The credit for the expansion and filling out of the Periodic Law, its extension to the other properties of the elements and the bringing of the various compounds of these elements into consideration also, has been almost entirely due to the skill and knowledge of Mendeléeff. He was bold and successful in his prophecy of new elements and their properties, and also as to

changes in properties then generally accepted. Many, though not all, of these prophecies have been fulfilled.

81. Meyer's Later Tables.—Lothar Meyer, in the later editions of his "Modern Theories of Chemistry" has given his table in a changed and improved form. He says of this table (3d ed. p 292):

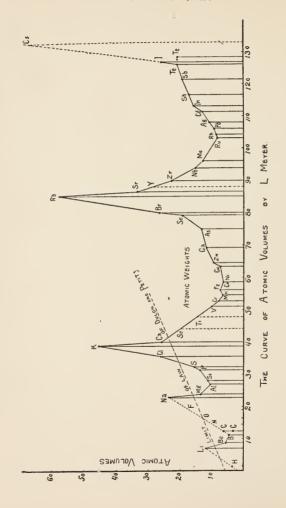
"If one will think of this table as rolled upon an upright cylinder so that the right side shall touch the left, thus nickel joining itself directly to copper, palladium to silver and platinum to gold, one will get as is easy to be seen, a continuous series of all the elements arranged in the form of a spiral and according to the size of the atomic weights. The elements which by this arrangement stand over one another form a natural group, or family, the members of which resemble each other in very unequal measure. In most of the groups four or five of the seven or eight members are more nearly related to one another than to the remaining three which again show a great similarity to one another. In the second vertical column, beginning with Li, the five light alkali metals are very much alike, while the three heavy metals agree with one another in many properties; with alkali metals, however, only in single points, as in the isomorphism of many of the compounds and in their ability to unite with a single atom of a halogen.

| 1.   | II.   | 111.   | IV.  | v.  | VI.  | VII.   |                    | VIII.   |                           |
|--|---|--|--|---|--|--|--------------------|---------|---------------------------|
| I.  I.i. 7.0I 15.98  Na 22.99 16.04  K 39.03 24.15  Cu 63.18 22.0  Rb 85.2 22.5  Ag 107.66 25.0  Cs 132.7  ? 165  Au 196.2  ? 2222 | Be 9.08 14.86  Mg 23.94 15.97  Ca 39.91 24.97  Zn 64.88 22.4  Sr 87.3 24.4  Cd 111.7 25.2  Ba 136.86  ? 170  Hg 199.8 | B IO-9 16.14 A1 27.04 16.93 Sc 43.97 25.9 Ga 69.9 19.7 ? Y 89.6 23.8 In 113.4 25.1 La 138.5 Yb 172.6 | C II.97 I6 Si 28 20 Ti 48 24 (Ge) 72 I8 Zr 90.4 27.4 Sn II7.35 23.8 Ce 141.2 Pb 206.39 | N<br>14.01<br>16.95<br>P<br>30.96<br>20.1<br>V<br>51.1<br>23.8<br>As<br>74.9<br>18.8<br>Nb<br>93.7<br>25.9<br>Sb<br>119.6<br>25<br>Di<br>145<br>Ta<br>182 | O<br>15.96<br>16.02<br>S<br>31.98<br>20.47<br>Cr<br>52.45<br>26.48<br>Se<br>78.87<br>17.0<br>Mo<br>95.9<br>30.4<br>Te<br>126.3<br>?<br>151 | F 19.06 16.31 C1 35.37 19.4 Mn 54.8 25.0 Br 79.76 19 ? 99 28 I 126.54 25 ? 152 | Fe 55.86  Ru 103.5 | Co 58.6 | Ni<br>58.6<br>Pd<br>106.2 |
| 222  | 226   | ? 230  | ? Th<br>231.96   | ? 234   | 210<br>?4<br>239·8   | ? 211  |                    |         |                           |

In a similar manner each of the following columns can be separated into two groups, clearly different and yet related to one another in certain particulars."

- 82. Meyer's Curve of the Atomic Volumes.—Meyer was the first to give a graphic representation of this law. He devised a curve intended to show the dependence of the atomic volumes upon the atomic weights. The atomic weights were taken as the abscissae, the atomic volumes forming the ordinates. The curve uniting the tops of these ordinates gave a picture of the changes which the atomic volume experiences with increasing atomic weight.
- 83. The Failure to Recognize the Importance of the Law.—As has been said, the Periodic Law soon attracted attention, but its importance does not seem to have been generally recognized at first, nor was it widely accepted as a law. In fact for several years it nearly dropped out of sight and it was only the lucky discovery of some new elements, thus fulfilling certain predictions of Mendeléeff, that brought it prominently before the chemical world. How long it would otherwise have laid unnoticed can only be guessed at.

In 1879, the London Chemical News translated from the Moniteur Scientifique and republished Mendeléef's article on the "Periodic Law of the Chemical Elements," because "considerable attention has been drawn to M. Mendeléeff's memoir in consequence of the newly discovered elements, gallium and scandium, being nearly identical with the predicted elements eka-aluminium and eka-boron."



Mendeléef said in his introductory note to the article mentioned:

"Although seven years have passed since these thoughts absorbed my attention; although other occupations have withdrawn my attention from the problem of the elements which was always getting nearer solution; in short, although I might wish to put this question otherwise than I did seven years ago, still I keep to the same firm conviction that I formerly had on the importance and value of the theorems on which my memoir is based. Several occurrences have aided to make some of the logical consequences of the Periodic Law popular.

1st. The law I announced has been considered as a repetition in another form of what has been already said by others. It is now certain that the Periodic Law offers consequences that the old systems had scarcely ventured to foresee. Formerly it was only a grouping, a scheme, a subordination to a given fact; while the Periodic Law furnishes the facts and tends to strengthen the philosophic question which brings to light the mysterious nature of the elements. This tendency is of the same category as Prout's Law, with the essential difference that Prout's Law is arithmetical and that the Periodic Law exhausts itself in connecting the mechanical and philosophical laws which form the character and glory of the exact science. It proclaims loudly that the nature of the elements depends above all on their mass, and it considers this function as periodic. The formula of the law might be changed; a greater appreciation of this function will be found, but I believe that the original idea of the periodic law will remain."

It is undoubtedly true, as has been said, "the discovery of gallium may be considered as the inauguration of the Periodic Law."

84. The Criticism of Berthelot.—From what has been said, it will be seen that one must look into the second decade after the announcement of the law for criticisms of it. Some of these may be quoted as showing the character of the reception accorded it.

An adverse criticism from Berthelot will first be given. The French have been especially slow in acknowledging the merits of the discovery. Somewhat strangely Berthelot's critique is placed in his Origins of Alchemy (145) where one would scarcely look for anything of that character, and so has escaped more general notice.

"It is known that certain general relations exist between the atomic weights of the bodies, their atomic
volumes and their different physical and chemical
properties. These relations were studied long before
the arrangement of the elements in parallel series.
They result from the absolute atomic weights and not
from any periodic differences. Yet, as these relations are
the immediate consequence of the "atomic weights, the
coincidences established between these come to light
again necessarily when we consider their atomic volumes
and all the other correlative properties of the chemical
mass of the elements.

"This circumstance increases the convenience of the new table. It brings no new proof of the existence of the periodic series. It is necessary to guard against all illusion in that direction. Let us examine the predictions deduced from the new classification. It is in this respect more than in any other that the system should prove interesting. In the arithmetical progressions which embrace each family of elements, it is seen that certain terms are lacking. Between S = 32 and Se = 79 there should exist two intermediate terms 48 and 64. In the same way between Se = 79 and Te = 128, two terms are lacking, 96 and 112. Evidently these are to be filled in by unknown elements and there is an opening here for research. But as the number of these is too great, the authors of the system, in haste to fill the gaps in each family, have interpolated elements already known which are manifestly strangers to the family: such as Mo inserted between Se and Te: W and U added in like manner to the series. To the series of Li = 7, H = 1 has been placed at the head and at the end Cu = 63, Ag = 108and Au = 197. All this trenches upon the fanciful.

"In the same way between CI and Br and between Br and I certain terms of the arithmetical progression are lacking. Here we have again hypothetical and to-be-discovered elements. Notice here that their properties are not undetermined. In fact the physical or chemical properties of an unknown element can be predicted and calculated when its atomic weight and family or analogies are given. This prediction is not a consequence of the theory of the periodic series. It results purely and simply, from the long-known laws and analogies which are independent of the new system.

"It is impossible not to draw the attention of the critic and of the philosopher to the convenient trick, by the aid of which the authors of the system have managed to include not only all known but all possible substances. This trick consists in forming their table with terms which do not differ by more than two units, terms so bound together that no new body, whatever it may be, can fall outside the meshes of the net. The thing is the more assured since the periodic differences often admit in their applications to known atomic weights, of variations of one to two units. We see that it is no longer a question of fractions of units which separate the multiples of hydrogen such as were raised as objections to the hypothesis of Prout and Dumas.

"Without excluding absolutely the conception of parallels, we must avoid attaching too high a scientific value to frames so elastic. Especially must we guard against attributing to it discoveries, past or future, to which it does not necessarily conduce in a precise and necessary manner. We might say, with all sincerity, that outside of the old natural families of the elements, known for a long time, there is little here but artificial groupings. The system of the periodic series has not, any more than the system of the multiples of hydrogen, furnished, up to the present, a certain and definite rule for discovering either the simple bodies found in late years or those which we do not yet know. None of these systems has given a positive method of fore-seeing, much less of synthetically forming, our elements.

"It is not that such systems have no use in the science; they serve to arouse and sustain the imagination of investigators. They submit, with difficulty, to rest

upon a purely experimental basis and push into the region of construction and of theories that spring from the desire for unity and causality inherent in the human mind. It would be too harsh, and useless besides, to wish to prescribe everything tentative of this nature. But such is the seduction exercised by these dreams, that it is necessary to guard against seeing in them the fundamental laws of our science and the basis of its facts, under pain of falling again into a mystic enthusiasm parallel to that of the alchemist.

"Such conceptions are on the one hand too narrow and it thus invites to elevating them too high. At bottom, those who invoke the multiples of hydrogen and the periodic series, bind everything to the conception of certain atoms smaller than those of the reputedly simple bodies. But if it comes to demonstrating that the equivalents of the actual elements are rigorously multiples, the one of the other, or more generally, multiples of certain numbers, forming the differences in determined arithmetical progressions, it results in this probable conclusion, that the actually simple bodies represent the unequal stages of condensation of the same fundamental material. This fashion of conceiving things has nothing which can be repugnant to a chemist versed in the history of his science.

"One can call to mind, as proofs, facts well-known to all and which are not without some analogy. Such are the multiple forms of carbon, an element which manifests itself in the free state in the most diverse forms and which gives rise to many series of compounds corresponding in a certain manner with each of these fundamental forms, as the compounds of an ordinary element correspond with that element. Carbon represents, in some sort, the common generator of an entire family of elements, differing in their condensation. One is brought to the same conclusion by a study of the hydrocarbons. The objection might be raised that the diversity of the properties of carbon should not be less than the diversity existing between the elements comprised in one family, those of the halogens or of the sulphur group, for instance. In reality S and Se never produce the same compounds in uniting with O, H, or N, and they cannot be regenerated by condensation of the most simple among them.

"To sum up, carbon viewed in its different states and degrees of condensation is equivalent in itself to an entire class of simple bodies. O, S, Se, and Te by the same reasoning could represent the different states of a common element. Further, ozone, a body of very simple properties, and comparable therefore to a true element, has been really formed of oxygen, its existence to a certain extent justifying the preceding conjectures.

85. Mendeleeff's Reply.—It is best to quote here, from his Faraday lecture, (181) Mendeléeff's reply to this criticism of Berthelot. This also gives the author's views of the many attempts to make use of the Periodic Law in speculations concerning the original form or froms of matter. We shall come across many such speculations in the remaining pages of this work.

"Feeling that spectrum analysis will not yield a sup-

port to the Pythagorean conception, its modern promoters are bent upon its being confirmed by the Periodic Law. It is evident that the illustrious Berthelot has simply mixed up the fundamental idea of the Law of Periodicity with the ideas of Prout, the alchemist, and Democritus about primary matter. But the Periodic Law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of an unique matter; and it has no historical connection with that relic of the torments of classical thought, and therefore it affords no more indication of the unity of matter or of the compound character of our elements than the Law of Avogadro, or the Law of Specific Heats, or even the conclusions of spectrum analysis. None of the advocates of an unique matter have ever tried to explain the law from the standpoint of ideas taken from a remote antiquity when it was found convenient to admit the existence of many gods or of an unique matter."

86. Ostwald's Criticism.—Ostwald has the following criticism of the Periodic Law on pages 126 and 127 of his Lehrbuch der Allgemeinen Chemie (149).

"The numerous and unexpected developments which the Periodic Law has given us as to the relations of the atoms, one to another, should not make us blind to certain difficulties which have arisen in its full application. Thus the discussion over the atomic weight of beryllium is not yet closed, since there are many reasons for not accepting the arrangement of the elements as given. Again elements are separated from one another which in the form of their compounds stand close together—as mercury and copper, with which it has more points of resemblance than with zinc and cadmium. Sodium is separated from the alkaline metals proper and placed with copper, silver, and gold. The silver here shows, at best, a relationship through the isomorphism of the water-free sulphate. Also the oxidation steps held up by Mendeléeff as characteristic or typical are neither the only ones, nor the lowest, nor yet the highest, indeed they are often unknown and incapable of existence.

"These objections are not raised to refute the Periodic Law. They are too few in number for that and stand opposed to too many favoring circumstances. They serve only to show that the law in its present form is only the beginning of a most promising line of thought. The idea of the analogy of the elements has still too much undetermined to permit of its definite use. There is still no numerical expression for it. Further, the relation of multiple proportions to the Periodic Law remains to be examined. Mendeléeff shows justly that the views predominating at present as to the valence of the elementary atoms has real meaning only for the carbon compounds and falls into constant contradiction in the case of the inorganic compounds. It is to be hoped that a theory of chemical compounds which will suit both branches of chemistry will be developed out of the relations of the multiple proportions to the Periodic Law. Lastly, it cannot be left without mention that in reflecting upon the causes of the Periodic Law the same metaphysical consequences press forward which have served as starting points for the hypothesis of Prout and have been somewhat supported by the approximate and partial agreement of the same with experiment. If the properties of the elements prove to be functions of the atomic weights, the thought lies near to seek in these also the causes of the same, and the assumption of a primal matter, whose different states of condensation define the differences of the elements, can hardly be set aside. These hypotheses are far reaching and far removed from sure foundation, but they accord with the general tendency of natural science."





## CHAPTER V.

DEVELOPMENT OF THE SYSTEMS.

1870-1880.

In the preceding chapter it was stated that but little was done to improve and extend the Periodic Law during the first years after its announcement. Its discoverers had dropped it for other work, Mendeléeff finding occupation in the study of the origin of petroleum and in various physico-chemical researches. Meyer (91) complained of the "present lack of system in inorganic chemistry" and appeals for the putting forth of greater efforts in the development of this branch of chemistry. He mentioned "the natural system of the elements arranged according to their atomic weights with which he and Mendeléeff had been busying themselves of late years" as a step towards this development. The natural system should be the principle of the classification of inorganic compounds.

87. A Return to Numerical Regularities.—We will find in the record of this decade, therefore, chiefly independent and new systems and a recurrence of numerical regularities such as were pointed out almost ad nauseam in the period immediately following the lecture of Dumas. It is strange to see how indefatigable chemists have been along this line and how many different "relations" they have discovered between the sixty odd numbers lying in the range of atomic weights between one and two hundred and forty.

There seems from now on a more marked tendency toward the search after laws underlying these relations. In the earlier periods the discovery of isolated "regularities" seemed to satisfy the investigator.

- 88. Growth in the Belief of the Unity of Matter.— There is also from this time forward a very evident increase in the number of adherents to the philosophic theory of the Unity of Matter. There is a revival of the Proutian Hypothesis under various forms. The composite nature of the elements is more widely and boldly stated and discussed. The last question of the century shows a revulsion to this old hypothesis in so far as it teaches that the elements are compound, though the part of it referring to the multiple relations existing between the atomic weights has been largely set aside.
- 89. Baumhauer's Spiral Arrangement.—In the year 1870, shortly after the appearance of the system of Mendeléeff and the table of Meyer, Baumhauer (90) suggested a mode of illustrating graphically the relationship between the elements and, possibly, the derivation, or nature, of the supposed simple bodies.

The fairly regular differences between the groups were given by Meyer in his earlier work. Baumhauer gives these differences as 16, 46, and 88-92. He then continues:

"A clear view of the elements and, with that, the explanation of many peculiarities, is first obtained when one arranges them in accordance with increasing atomic weight in the form of a spiral, giving hydrogen the central position. Similar elements fall under one another. The ring-formed series in the spiral are called central, those reaching from center to periphery are radial. For the sake of greater simplicity seven chief radials are assumed, some of which are again split up into several others. Between the radial and central series numerous transitions show themselves which are to be explained by the preponderating influence of neighboring elements. Only when the relations to all neighboring members of the system appear for each element at the same time and with equal intensity will the whole furnish a perfect scheme.

"The relations to neighboring elements can be many and since they cannot be quantitatively determined, it is difficult, proceeding from the chemical properties of the element, to assign it its proper place in the system. Generally, however, the position of an element relative to the others can be determined by a closer observation of the clue given by its characteristics. The principle followed can be outlined as follows: Each element holds a position determined by its chemical characteristics, as a summary expression of which the atomic weight may be regarded, either upon the continuous series of a spiral arranged according to increasing atomic weight or between the rings of the same. In the last case, as well as by each interposition upon the spiral itself, the chemical nature and the atomic weight of the element in question is dependent upon the nature and the atomic weight of neighboring elements. Thus one can calculace atomic weights for any blank positions upon the

spiral where an element is lacking. This can be only imperfectly done after passing the atomic weight 137 as so many of the vertical and side neighboring elements are lacking.

"The atomic weight and the chemical nature of an element stand in close connection with one another. Still this connection is not usually a simple one. On the contrary, the atomic weight of an element is composed of the atomic weights of others in just the measure in which its properties show themselves to be a complex of other elements. This idea can be brought under the general formula

$$A = \frac{lB + mC + nD \dots}{l + m + n \dots}$$

where A = the atomic weight of an element, B, C, D atomic weights of related elements, l, m, n certain coefficients. These last express the ratio of the magnitude of affinity of A with the elements B, C, D... According to this formula, quite different elements can have similar atomic weights whereby B, C, D, as well as l, m, n, have a different meaning in each separate case. Like elements also have almost identical weights where B, C, D, as well as l, m, n, change only in slight degree.

"The form of a spiral was chosen for the graphic representation of these facts only after many vain attempts at arranging the element in other ways which would express the facts equally well. The typical elements fall upon the spiral and their atomic weights form an increasing series. They show relationship to one another and may perhaps in part be referred to still sim-

pler types. The elements appearing as medial members can be recognized from their many-sided characteristics.

"In this table the relation of the elements to one another is indicated by arrows in the more difficult cases.

"The most distinguished chemists are united in the opinion that there exists one or a few primal elements and that our elements are at most modifications or combinations of these. This idea is expressed in the table in the reduction of the complicated elements to certain types, and thus each series is represented by its initial member which has the lowest atomic weight. The other members differ from the first in their density. Almost without exception the specific gravity increases from the center to the periphery of the spiral. We can therefore assume that all elements of any one typical series are only definite functions of the first member. Their atomic weight is gotten by the addition of a number given by the building of the spiral.

"One can go a step further and look even upon these initial members as peculiar and to a certain degree individualized modifications of one and the same primal matter. This, however, is of course only speculation."

The diagram follows and needs no further explanation. Its resemblance to that of Hinrich's will be noted.

90. Additional Work by Newlands.—In 1872 Newlands published his first priority claim (86). A little later, in a short note, (87) he drew attention to the occurrence of the fourteen principal elements, which are most widely distributed and which appear to be essen-

tial to vegetable and animal life. He observed that they comprise two representatives of each of the chief chemical groups. In this he classed hydrogen and chlorine together and aluminium and iron.

In 1873 he made another priority claim before the London Chemical Society. In 1875 he gave another table to be used in text-books as a substitute for the old alphabetical lists, which have been hard to displace. In this he included the ordinal-number, to which he continued to attach importance, the symbol, the atomic weight, and the difference between each atomic weight and the one immediately preceding it. He drew attention to the recurrence of analogous elements at every eighth interval and repeated his former comparison to the octaves in music. When the table was given a horizontal arrangement, in sevens and in sixteen columns, he remarked upon the quantivalence of the elements thus exhibited.

In 1878 (104) Newlands gave a table comparing the atomic weights derived from four different standards: Hydrogen, 1; Sodium, 10; Chlorine, 15, "nearly"; and Carbon, 5. Comparisons are made with the ordinal numbers. These need not be commented upon and the following brief notes of his will be passed over with bare mention.

- 1. He believed the atomic weights to be invariable.
- 2. It is possible that elements of higher atomic weight might contain those of lower atomic weight, but not the reverse.
  - 3. If we view all matter as really composed of various

modifications of one elementary substance, consisting of physical atoms, we may regard the atomic weight of each element as expressing the relative number of physical atoms contained in the chemical atom. The same number of physical atoms differently arranged might form two or more distinct elements which might then be regarded as isomeric. Perhaps cobalt and nickel are thus related.

- 4. With regard to Prout's law; the number of elements whose atomic weights approach, within experimental errors, to exact multiples of hydrogen is far greater than it should be on the theory of probabilities.
- 5. It sometimes happens that the atomic weight of one element, when doubled, gives a number identical, or nearly so, with the atomic weight of another.
- 6. It frequently happens that out of three elements having common properties, the atomic weight of one approaches the mean of the other two, as in the well-known triplet groups or triads.
- 7. Two atomic weights, taken from the lower part of the series, when added together frequently equal the atomic weight of some other element, though no general rule seems to be applicable to such cases.
- 8. Taking the three lowest known atomic weights, those of H, Li, and Be; many of the higher atomic weights may be arithmetically derived from them by various combinations.
- 9. Taking a certain number of elements whose weight may be supposed to be consecutive, say the twenty-eight first, and arranging them in two columns, the first half

in order of the atomic weights and the second in reverse order, nearly a constant quantity will be gotten by adding together the corresponding members of the two columns, if the atomic weights corresponded to the natural order of numbers, or to some multiple of such order. As a matter of fact the numbers obtained vary considerably.

- ro. No simple relation could be worked out of the atomic weights under any other system than that of Cannizzaro, and if we attempt to introduce various equivalents of one element into the table they seem out of place, as do also the combining weights of quasi-elements, such as ammonium or cyanogen.
- 11. If any data, as specific heats or vapor densities, should prove ultimately to be without exception, either directly or inversely as the atomic weights, a list of elements arranged according to such data would, of course, also show a Periodic Law.
- 12. Although all the elements yet discovered appear to take their places in accordance with the Periodic Law, it is quite conceivable that various series of elements may exist not very simply related to each other.

Newlands' mind ran on numbers—a mania for numerical relations. It was impossible for him ever to have developed the Periodic Law.

91. The Synoptical Table of Gibbes.—A "Synoptical Table of the Elements" was published by L. R. Gibbes in 1875, in the proceedings of the Elliott Society of Charleston (95). It purported to be a table prepared, two or three years before, for the illustration of his lectures to

|          | A1 = 27.5<br>Y = 61.7<br>Ir = 64   |  | - I          | - 2               | <del>ا</del> 3                              | <u> </u>                                     |           | ea .    |
|----------|--|--|--------------|-------------------|---|--|-----------|---------|
|          | A1 = 27.5 - Y = 61.7 $Ir = 64$   | Li = 7<br>Gl=9.3<br>B=11                                 |              |                   |   |  | Α.        |         |
|          |  | Li=7 Na=23 K=39 Gl=9.3 Mg=24 Ca = 40 -B=11               | F = 19       | 0=16              | N=14 P=31                                   | C=12   | в.        |         |
|          | Cr = 52.5  | •  | C1 = 35.5    |                   |   | Si = 28                                      | c.        |         |
| I = H    | Cr = 52.5; Mn = 55; Fe = 56; Co = 59; Ni = 59; Cu = 63.5; U = 120<br>Zr = 89.5; Ce = 92; Le = 92; D = 92; Zr = 112; 72 = 115.7<br>Ru = 104; Ro = 104; Pd = 106 - Pt = 197: Ir = 197  | Zn = 65  |              | Cr = 52.2 Se = 79 | V = 51.3   As = 75                          | Ti = 50                                      | D.        |         |
|          | Mn = 55; Fe = 56; Co = 59; Ni = 59; Cu = 63.5; U = 120<br>Zr = 89.5; Ce = 92; Le = 92; D = 92; Zr = 112; 72 = 115.7<br>Ru = 104; Ro = 104; Pd = 106 - Pt = 197: Ir = 197   | Rb = 85 Ag = 108 Cs = 133<br>Sr = 87.5 Cd = 112 Ba = 137 | Br = 80      |                   |   |  | Ė.        | SERIES. |
|          | Co = 59;<br>Le = 92;<br>o = 104;   | Ag = 108 Cs = 133<br>Cd = 112 Ba = 137                   |              | Mo = 96 Te = 128  | Cb = 94                                     |  | <b>F.</b> |         |
| . Hg     | Ni = 59; $D = 92;$ $Aightarrow Pd = 106 - 106$ | Cs = 133<br>Ba = 137                                     | I = 127      | Te = 128          | Sb =: 122                                   | Sn = 119                                     | G.        |         |
| Hg = 200 | Cu = 63.5<br>Zr = 112;<br>- Pt = 197   |  |              |                   | W = 184                                     | Ta = 182                                     | HI.       |         |
|          | 55; Fe = 56; Co = 59; Ni = 59; Cu = 63.5; U = 120<br>1.5; Ce = 92; Le = 92; D = 92; Zr = 112; 72 = 115.7<br>Ru = 104; Ro = 104; Pd = 106 — Pt = 197: Ir = 197  | T1 = 204<br>Pb = 207<br>Bi = 210                         |              |                   | Os = 199                                    | Au=196.6                                     | ж.        |         |
|          | Iron Gr. Platinum Gr.  | T1 = 204 Kalium Gr. Pb = 207 Calcium Gr. Bi = 210        | Chlorine Gr. | Sulphur Gr.       | Sb =: 122 W = 184 Os =: 199 Phosphorous Gr. | Sn = 119 $Ta = 182$ $Au = 196.6$ Silicon Gr. |           | GROUPS. |

his class. It is mentioned thus in detail because the main interest attaching to it is that a professor in a remote and small American college should, a few years after the appearance of Mendeléeff's paper, have worked out for himself, evidently in ignorance of the work of Meyer and Mendeléeff, some of the most important principles of the Periodic Law. The evidence of this ignorance is presumptive; first, because his table was very crude and certainly would scarcely have been offered to his classes had the author known of the much superior ones which had just appeared; secondly, he carefully mentioned all authorities known to him and upon whom he had drawn in the construction of his table. He forestalled two or three later authors in his methods of graphic representation of the law.

The relations the author desired to exhibit in his synoptical table were: to show the groups of elements as at present recognized, the atomic weights of each element as now adopted, the character of each, as artiad or perissad, the valence, and the electro-chemical character. In the discussion of his table, he remarked:

"Now reading each series downwards, beginning with A, and following the order of the letters (see table) a remarkable regularity will be observed in the succession of the numbers, as far as the arrangement has been now described, yet with gaps unfilled by numbers in several of the groups."

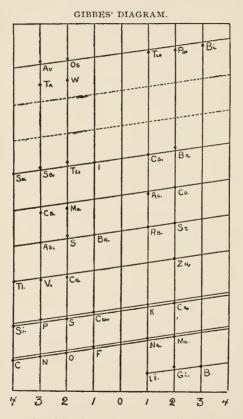
Influenced and guided by this order of succession he made several changes in the groups as given by Barker, (whose Text-Book of Chemistry he was following.)

The author observed that in this table the continuity or regularity in the series of number is very striking; the perissad or artiad character of each series is preserved throughout; also, with a few exceptions the prominent degree of equivalence is well preserved and indicated; the electro-chemical character, in addition, is very fairly presented.

Any one series, he said, may be expressed by an equation P = Qa where a is the number with its sign, which expresses the atomicity. In series A it is approximately 5 + 2a, in series B, 20 + 2a, in series C, 30 + 2a, etc. The numbers in the first three series A, B, C may be represented very closely by an arithmetical series whose first term is 7 and equi-difference 2. The average difference for numbers on the same line in series B and C and also in A and B is 16; for C and E, the difference is about 46 and between E and G about 48 (3  $\times$  16.) The occurrence of Dumas' triads and his parallelism in the table are pointed out. The recurrence of multiples of eight in the groups and in the differences between the series is also remarked upon, showing the influence of the earlier workers upon the author.

In his diagram he gave upon the horizontalaxis, right and left from the center, the positive and negative electricities as abscissae. The atomic weights are laid off as ordinates upon the vertical axis rising from a zero atomicity. This gives the elements in an ascending scale of atomic weights though they are broken up into series. With very acute reasoning and insight Gibbes showed that the three series may be exhibited in continuity as

one, that is by the use of an Archimedean spiral whose radius vector increases by 16 units in one revolution.



This is the helix of Lothar Meyer, and of De Chancourtois, and the spiral of Mendeleéff. His diagram will on ex-

amination be seen to be based on the same principles as those of Spring, Reynolds, and Crookes.

The author went further and anticipated some of the work of Haughton. He observed that no linear equation could be constructed to give more than rude approximations to the atomic weights, and that to construct curves, two points of inflection of contrary curvature must be given. These are the serpentine cubics afterwards given by Haughton. He cautioned against laying too much stress upon such arithmetric and geometric exercises.

It seems remarkable that, with so imperfect a table, so much of the later work done with the perfected tables, given by the authors of the Periodic Law, should have been anticipated, especially when we notice how slight was Gibbes' idea of periodicity. He gave in his table seven groups, it is true, four negative and three positive, but they are very poorly filled outandhe showed no completed period of seven in the entire table. His "regularity" can scarcely refer to periodicity.

He found something of what Meyer calls Double Periodicity. Under each of the groups of his table he noted th at two sub-groups might be distinguished. These are not clearly shown on every line but taking line 2 the series B, D, F, gives one secondary sub-group; C, E, G, gives the primary sub-group. In a note he said that Hg could only find a place in series H, I line 2. He had not so inserted it because of the novelty of its finding a place in the calcium group. If this be done and it be called a member of the magnesium sub-group, then the difference between its atomic weight and that of cadmium,

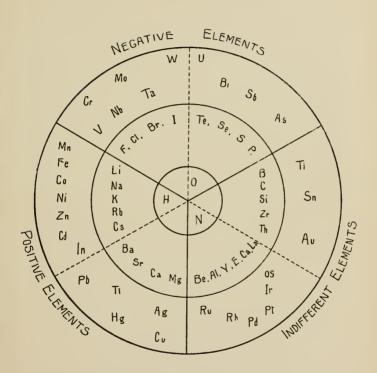
namely 88, will be exactly the same as between those of Mo and W and between those of Cb and Ta. But then the continuity of sequence would have been broken by an inversion, the number 200 exceeding some of those that followed it.

92. The Concentric Ring Arrangement of Wiik.— In the same year that this article of Gibbes was published, Wiik (96) made an attempt at grouping the elements. He first gave a critical notice of the arrangements of Mendeléeff, Meyer, and Baumhauer. In his own work he laid especial stress upon the electro-chemical theory of Berzelius. Much of it is based upon mineralogical data and conceptions.

In his arrangement of the elements he made use of three concentric circles which contained the three series:

- 1. Non-Metallic or Primary Elements.
- 2. Half-Metallic (including metalloids) or Secondary Elements.
- 3. Characteristically Metallic (heavy) or Tertiary Elements.

These circles were divided by three radii into positive, negative and indifferent elements with H, O, and N, respectively, as initial elements for each electro-chemical group. He suggested that the oxides Be<sub>2</sub>O<sub>3</sub>, ThO, etc., would be in better accord with his arrangement than the ones known; also certain changes in the atomic weights. In another table he brought out the fact that the differences between the atomic weights were frequently multiples of 16, 14 or 1 by 3 or 6 and also that many of them were multiples of 12 or of 4. These differences he thought



closely related to the ozone and antozone of Schönbein. From this he was led to consider the primal elements. In oxygen, which is indifferent, he found the presence of +O=4 and -O=12, the same numbers noted above. He found a further relationship between the sums of the atomic weights of the indifferent and electro-positive and electro-negative elements and their differences. The specific gravities and melting points were also considered in another table.

His theory as to the genesis of the elements was built upon Laplace's Theory of the Heavens, Berzelius' Electro-Chemical Theory and Edlung's Theory of Electricity. The ether is supposed to be at a different electric potential at different points and if it should then segregate, it would take on a different character at one point from that at another. For example, it might be in excess at one point and deficient at another. Suppose these were in the ratio of 3 to 1, then —O and +O would be formed where the ratios are 12 to 4, etc. The ether thus goes over into matter and, when of the proper mass, would yield all the elements.

A last table is given in which the elements are arranged in the form of a V, thus:



Each half contains 31 elements and they are united by Li. One half has the heavy, the other the light and non-metals.

The occurrence of the elements in the outer layers of the earth's crust was considered and lastly the applicability of the theory to the entire inorganic world.

- 93. The Primal Element of Simmen.—Simmen (97) formed an hypothesis of a primal element and assumed that the atoms of the supposed simple bodies were built up of the atoms of this primal element. As each primal atom had the same weight, the difference in the atomic weights of the elements was due to the different number of primal atoms brought together in each. Besides the number, the form, size, etc., of the primal atoms exercise their influence upon the properties of the elements; thus he thought the valence dependent upon the form of the atom. Chemical force was looked upon as identical with the force of attraction. This diminished with the square of the distance but never entirely disappeared.
- 94. Waechter's Numerical Regularities.— In 1878 there was a paper by Waechter (106) in which the old question of the numerical regularities was again taken up. The regularities recorded were:
- 1. A table beginning with the first period of Mendeléeff and giving the elements in the different groups whose atomic weights differ from those of the first seven by 16 or a multiple of 16. Thus the horizontal lines in the table contain elements of the same valence whose atomic weights increase by a multiple of 16 approximately.
- 2. The following can be shown true of these elements. The arithmetic mean of the atomic weights of two ele-

THE TABLE OF WAECHTER.

| a+8.16  |                                 | :                              |                     | :                        | Bi = 138.1                      | Ba=137.166                 | Cs=133.036                               |
|---|---------------------------------|--------------------------------|---------------------|--------------------------|---------------------------------|----------------------------|--|
| a+7.16  | 1 =120.850                      | Te=128.                        | Sb=122.265          |                          | :                               | •                          |  |
| a+5.16  | :                               | :                              | :                   | :                        | :                               | :                          | <u>:</u>                                 |
| a+5.16  | :                               | •                              |                     | :                        | Ce =92.50                       | Sr =87.51                  | Rb=85.36                                 |
| a+2.16   a+3.16   a+4.16   a+5.16   a+5.16   a+7.16 | Br=79.952                       | Se=79.43                       | As=74.915           | 76.                      | :                               | :                          | •  |
| a +3.16   | :                               | :                              | :                   | :                        | :                               | :                          | :  |
| a+2.16  | :                               | :                              |                     |                          | V =46.2                         | Ca=39.974                  | K =39.137                                |
| a+1.16  | Univalent F = 18.96 Cl = 35.457 | $Bi \dots O = 16$ $S = 31.978$ | N =14.044 P =31.045 | Tetra C =11.97 Si =28.05 | Bo=10.8 $A1 = 27.48$ $Y = 46.2$ | Be= 9.3 Mg=24.38 Ca=39.974 | Uni $ I_i  = 7.022  Na=23.043 K=39.137 $ |
| a   | F =18.96                        | 0 = 16                         | N =14.044           | C =11.97                 | Bo=10.8                         | Be= 9.3                    | $L_i = 7.022$                            |
| Valence.  | Univalent                       | Bi                             | ľri                 | retra                    | ľri                             | Bi                         | Uni                                      |

ments with equally intense but opposite affinity are nearly equal to one another. That is, they equal 76. This, the author said, corresponded to a hypothetical element forming the middle of the series.

$$\frac{F + Cs}{2} = 75.998 : \frac{O + Ba}{2} = 76.583 : \frac{N + Di}{2} = 76.272 :$$

$$\frac{I + Na}{2} = 74.99 : \frac{Te + Mg}{2} = 76.19 : \frac{Sb + Al}{2} = 75.372.$$

Further laws as to the affinities of these elements, the melting points and boiling points, the specific heats, the specific gravities etc., are given. His table is given on page 136.

95. Lockyer's Hypothesis as to the Compound Nature of the Elements.—A paper (107) read, in the year 1878 before the Royal Society, by Lockyer upon a working hypothesis that the elements are in reality compound bodies created a great deal of comment and discussion. This paper may be summed up as follows:

While engaged upon the task of mapping the spectrum of the sun with the Frauenhofer lines and comparing them with the spectra of known elements, the author met with many facts which led him to propound the hypothesis that the elements were after all compound bodies and not simple. The spectroscopic evidence led him to believe that there was a decomposition of the elements brought about by the intense heat of the sun and other bodies.

The hotter a star, the more simple its spectrum seems to be. Thus Sirius, which is at least one of the brightest of stars, furnishes a spectrum showing only very thick hydrogen lines and a few very thin metallic ones, characteristic of elements of low atomic weight. And this is true of other very bright ones. The cooler ones, as our sun, contain a much larger number of metallic elements but no non-metals, and the coolest furnish band spectra, characteristic of compounds of metallic with non-metallic elements. These facts appear to meet with a simple explanation if it be supposed that, as the temperature increases, the compounds are first broken up into their constituent elements and that these elements then undergo dissociation into elements of lower atomic weight.

With regard to the hydrogen spectrum, Lockyer stated that he had obtained evidence leading to the conclusion that the substance giving the non-reversed line in the chromosphere, which had been termed helium, and not previously indentified with any known form of matter, and also the substance giving the 1.474 or coronal line, are really other forms of hydrogen, the one more simple than that which gives the *H*-line alone and the other more complex than that which gives the *F*-line alone.

96. Berthelot's Discussion of Lockyer's Hypothesis.—Shortly after the publication of Lockyer's Hypothesis there appeared (108) the following criticism from Berthelot: "I think the hypothesis of a progressive decomposition of all substances through increasing temperature, bringing first compound substances to the elements known to chemists, and then again to yet simpler elements, is to be enunciated with reserve.

"Simple substances, as we know them, bear certain positive characters not belonging to compounds, e.g., the

relation between specific heat of a substance, the gaseous density and atomic weight relation, independent of temperature.

"There is between the physical properties of the elements and those of their compounds, a singular opposition. This opposition does not at all prove the theoretical impossibility of decomposing our actual elements, but it better defines the conditions of the problem, and leads us to think that the decomposition of our simple substances, if it may occur, must be accompanied by phenomena of quite a different order from those which have hitherto determined the destruction of our compound substances."

97. Crookes' Views as to the Same.—At the same time (109) there was the following expression of opinion from Crookes: "Even at present, therefore, until some part is shown to be irreconcilable with Mr. Lockyer's views we consider ourselves perfectly justified in giving them our provisional adhesion, as a working hypothesis to be constantly tested by reference to observed phenomena."

Crookes went further and heralded Lockyer as the "Darwin of the inorganic world."

98. Zaengerle's Numerical Relations.—In 1871, Zängerle (88), to whose work we shall have to refer again, had come to the conclusion that "all of the atomic weights are the sum of two or three products, the first of which is gotten by the multiplication of one of the six fundamental numbers by a whole number, whilst the second, or the two others, are gotten by the multiplication of one or two of the six difference numbers by also whole

numbers." He found it necessary in the use of these numbers to allow himself very wide latitude.

99. Lersch's Numerical Relations.—Lersch (112), in criticising the work of Zängerle, remarked: "By the combination of such elastic products it is naturally extremely easy to obtain any desired atomic weights, especially if one neglects the decimals." Lersch endeavored to find out for several of the groups some one "fundamental value" or number of which they are all exact multiples. For instance A1 =  $13 \times 2.1$ : La =  $44 \times 2.1$ :  $Cr = 25 \times 2.1$ :  $Th = 55 \times 2.1$ :  $Ce = 66 \times 2.1$ . Pursuing this idea further he made use of one-half of the square root of one of the atomic weights in a group as the fundamental value; thus, the square root of the atomic weight of Cu is 7.9379; this divided by two is the fundamental value, or g; 27g = Ag; 28g = Cd; 52g = Pb. In other groups a difference number, d, is made use of. Thus:

| Lithium group                 | g=7. | Magnesium group           | g = 8.  |
|-------------------------------|------|---------------------------|---------|
| Li 7                          |      | Mg 8                      |         |
| Na 7 <b>+</b> 16              | = 23 | Mg 8+15.95                | = 23.95 |
| K 7+2×16                      | = 39 | Ca 8+15.95                | = 39.9  |
| $Rb_3 \times 7 + 4 \times 16$ | = 85 | Sr $3\times8+4\times15.8$ | = 87.2  |
| Cs $3\times7+7\times16$       | =133 | Ba 3×8+7×16.11            | =136.8  |

Various groups can be built up by the use of the fundamental and the difference numbers. Thus:

```
Lithium group has g = 4 and d = 1.174 (=
                 " g = 4 " d = 1.174 " g = 5 " d = 1.174
Magnesium "
             "
Nitrogen
                 " g = 8"
Oxygen
             "
                                d = 1.174
                 " " = 9 "
             66
                                d = 1.174
Berv11
                 " g = 7 "
                                d = 2.486 \text{ (almost } \sqrt{38} \text{)}
Fluorine
             66
```

The various atomic weights may then be worked out as follows: 4g + 6d for Na; 33g + 4d for Ba; 4g + 17d for Fe, etc.

Lersch then discussed the relation of the square root of the first member to the other members of the group. He found that when one-half this square root is multiplied by 16 the second member of the group is obtained. For the others he failed to show any note-worthy regularity. To improve the results he made use of some quite complex formulas. He next examined the relations existing between the square roots of the atomic weights of the different members of a group. These are not simple. The cubic roots, he said, yield no satisfactory relations.

His next effort was to discover some relation by taking the four members of a group as equal to 1000 and then apportioning this among them according to the ratio of their atomic weights. These numbers are then compared in various ways. The squares of the atomic weights are then examined. Thus he finds  $(12^2 + 28^2)2\frac{1}{2} = 48^2$  nearly. That is for the carbon group. For

K, Rb, and Cs he gets 
$$\frac{(39^2 + 85.2^2)_4}{2}$$
 = 132.5, etc. At

the close of his paper upon the numerical relations to be observed in the system of planets, he remarked that the ratio of the atomic weights of fluorine and chlorine to one another approached very closely to that of the distances of the sun from Mercury and Venus. And so the ratio between fluorine and bromine approached that of the distances from Mercury and Mars. Other chemico-

astronomical ratios are given, all of which seem decidedly "bizarre" to use the language of one of his critics.

100. Zaengerle's Primal Elements.—In 1882, Zängerle (121) attempted to account for the regularities in the properties of the elements upon the ground of several primal elements and then later upon the assumption of one. He divided the elements into various groups and distinguished three series in each group: one electro-negative, one intermediate and one electropositive. In the intermediate stood the fundamental or type-element, in the two others the atomic weight increased from element to element by a definite increase. These two increments and half the atomic weight of the type represent the atomic weights of the three primal elements forming the bases of each group. Take, for example, the carbon group: The atomic weights forming the basis are  $A = \frac{c}{2} = 6$ ; E = 21; and I = 22. Then one gets the intermediate series  $C=A_a$ ; Sn  $=A_a+E_a+I$ ; Th  $=A_a+E_a$ +  $I_{i}$ . Electro-negative group, Si = A + J;  $Ti = A + J_{i}$ ;  $Nb = A + J_4$ ;  $Ta = A + J_8$ . Electro-positive series  $Zr = A + E_{\perp}$ 

Thus one sees that only in the intermediate series do all three primal elements make their appearance. Since J is negative and E is positive, the differences in the electro-chemical behavior can be ascribed to the relations of A, E and J to one another.

Leaving these three primal elements, Zängerle went, beyond the reach of all experiment, to a single original element out of which all the others are supposed to be formed. This is the hypothetical ether of space and to

it he assigned the atomic weight 0.0001. The differences between the atoms, as we know them, depend either upon their formation out of unequal amounts of this ether, or upon a different arrangement of the atoms, or finally upon differences in the directions and number of the vibrations of the primal atoms. These primal atoms form condensations of three grades. The condensations of the first grade are the molecules of the primal matter. Out of these molecules condensations of the second grade are formed, namely the atoms of the various elements. His further conception is something like the composite elements of Brodie (p. 70). He spoke of some of the elementary atoms as being formed out of the primal molecules combined with  $\alpha$ -,  $\beta$ -, or  $\gamma$ -oxygen, which oxygen is to determine the periodicity. Condensations of the third grade are finally the molecules of the elements and the compounds. The system of symbols used is somewhat like that of Brodie.

Now upon these hypotheses just mentioned, Zängerle built up a natural system of the elements and gave a very full table, which is here copied in part. All the elements are divided into hydrogenoids and oxygenoids and these two main groups fall again into the six natural families; that of hydrogen, of beryllium, of boron, of carbon, of nitrogen and of oxygen. Each family has several groups, at the head of each of which a typical element stands. Thus in the hydrogen family there are the types H, Na, and Mg with their groups. These are again separated into series and those with odd atomicity fall in one series and those with even in another. The

31.95 74.95 119.88

= 209.78

 $= N_7 Oa_7$ 

Bi.

## ZAENGERLE'S PRIMAL ELEMENT TABLE.

| .000                    | ial molecule.                               | II. Oxygenoids.  | 5. Nitrogen-elements. | $n = h_{201} + O_8 = 4.67.$   | s of the elements.                                 | $N = n_3 = 14.01$ .      |  |
|-------------------------|---|------------------|-----------------------|---|--|--------------------------|--|
| Primal atom: U = 0.000. | Condensation first grade = primal molecule. | I. Hydrogenoids. | 1. Hydrogen-elements. | $\mathrm{Uh} = \mathrm{U}_{i} = \mathrm{0.0004h} = \mathrm{Uh}_{13} = \mathrm{0.01.}$<br>$\mathrm{Li} = \mathrm{Uh}_{381} = 2.336.$ | Condensation second grade = atoms of the elements. | b. $L_i = li_3 = 7.01$ . |  |
|                         | teral<br>ula.                               | nsO<br>mrol      |                       | ı   |  | ×                        |  |

 $= N_2OaOb$ =  $N_3OaOb$ =  $N_4Oa_4$ As :: A. Series with elements of odd atomic weights.

 $Pb = Li_8Oa_2Ob_7 = 206.72$ Mg = LiOb  $Zn = Li_2Ob_3$   $Cd = Li_4Ob_6$  $\begin{array}{ll} \text{Cu} = \text{Li}_1, \text{Oa}_3 & = 61.90 \\ \text{Ag} = \text{Li}_1, \text{Oa}_5 & = 107.84 \\ \text{Au} = \text{Li}_1, \text{Oa}_7 & = 195.72 \\ \text{Hg} = \text{Li}_8, \text{Oa}_9 & = 199.68 \\ \text{T1} = \text{Li}_8, \text{Oa}_7, \text{Ob}_2 = 203.72 \end{array}$ = 22.97 = 61.90 = 107.84 = 195.72 = 199.68RnO RnO<sub>3</sub> RnO<sub>5</sub> RnO<sub>7</sub> RnO.

B. Sories with elements of even atomic weights.

|   | 50.61                       | $\frac{NN}{N} = \frac{N}{N} = N$ | 93.06                | = 182.40          |
|---|-----------------------------|--|----------------------|-------------------|
|   | l)                          | ٦  | 25                   | 1)                |
|   | $Vd = N_4Oa_2$              | 2  | 12 Ca2               | $Ta = N_{10}Ob_8$ |
|   |                             |  | ]                    | II                |
| 0   | PΛ                          | , The state of the   |                      | Ta                |
| D. Serves with comments of com morning with | 39.68 $Ca = LiOaOb = 39.93$ | $Sr = Li_{16}OaOb_2 = 87.23$   | Ba = 14.0b. = 136.81 |                   |
| 20 524 1                                    | 39.68                       | 85.23  | 07 071 -             | 61.001            |
|   |                             | 11   | Ī                    |                   |
| 7   | $K = L_iOa_2$               | $\mathrm{Rb} = \mathrm{Li}_{16}\mathrm{Oa}_3$  | Ce - 13 Oa           |                   |
|   | 00                          | NIIO2  | KnO <sub>4</sub>     | RnO <sub>8</sub>  |

different atomicity arises from the combination of a typical element with one of the primal molecules. Oa 15.96, or Ob 16.96, or Oc 17.96. The series differ in their electrochemical character. Elements of uneven atomicity are electro-negative those of even atomicity are electro-positive and further the hydrogenoids are positive towards the oxygenoids.

Zängerle maintained (88) that the properties of the elements are in gradations and that these gradations correspond to the atomic weights. Ten such gradations are observed. The atomic weights of the negative and positive elements yield the same differences from gradation to gradation with few exceptions. These differences range between 16 and 24 and may be calculated by the formula  $(B-\frac{a}{2})$ : d where B= atomic weight of any chemical element a= atomic weight of the primal element and d= gradation.

The atomic weight of any element may be calculated by means of the formula  $\frac{a}{2} + dx$  where a = atomic weight of the primal element, d = gradation and x = differential of the series.

A portion only of Zängerle's table can be given as a specimen of his method of grouping; namely, out of the hydrogen family the Na and Mg groups, and from the oxygenoids the nitrogen group. It will be seen that here, there is no talk of one single series of elements with increasing atomic weight. The atomic weights increase only in the series, as a rule in the horizontal succession. The chemical and physical properties of the elements stand in a simple relation to one another; they change

in periods with the atomic weights. The elements of any series are for the most part homologous compounds of the primal element with oxygen, hence their character changes with the contents of oxygen. At the same time it must be considered whether the oxygen atoms are in even or uneven numbers combined with the primal element. For instance: Li; LiOa = Na; LiOb = Mg; the character of Li not yet much altered. LiOa<sub>2</sub> = K; LiOaOb=Ca; slight change to be noted. Li<sub>2</sub>Oa<sub>2</sub> Cu; Li<sub>2</sub>Ob<sub>3</sub>=Zn; complete change of character.

Zängerle further gave these rules:

"In the case of the hydrogenoids the basic character increases with increasing atomic weight in the electropositive series, the acid in the electro-negative, whilst by the oxygenoids the opposite is true. In any series the atomic volume of the elements increases in simple ratio with the atomic weights. The melting points and the boiling points show themselves joined to the atomic weights in the same way but in different methods in the different series."

Zängerle claimed for his system the possibility of predicting unknown properties of known and unknown elements, the prediction of these elements themselves, the correction of their atomic weights and other constants. He gave a second table in which he endeavored to make clear the connections between the properties of the elements and their atomic weights.

Gretschel and Bornemann (135) seem to regard the work of Zängerle as giving "more or less clear echoes of the hypothesis of Prout, the ideas of Brodie and the periodic system of Mendeléeff. The regularities and relations of the latter are repeated and it is in a measure an elaboration of it.''

Zängerle concluded his work with the hope of soon bringing experimental proofs of his theories.

101. The Criticism of Meyer and Seubert. - After speaking of Zängerle and his hypothesis (147) Meyer and Seubert say: "Speculations of this kind are far removed from any possibility of experimental proof, and can therefore never be expected to receive from it any support. Nor can we ever hope to receive any essential extension of our knowledge in respect to primal matter through a more accurate establishment of the atomic weights; the next important progress will rather be brought about by the decomposition of the elements into a similar substance, differing from them however, which may be the primitive matter itself, or a condensation product of it. The solution of this question, that is, the decomposition of all the elements into one and the same original substance, we can hardly ever expect to accomplish.

"The universal ether, with an atomic weight of 0.0001 (H=1), has been assumed as the primitive substance of which all other elements were formed. The atomic weights of all other elements must of course be whole multiples of this, since none of them have been accurately determined to the fourth decimal place, while many are certain only to the first or second place, and some only to units of hydrogen."

102. Meyer's Ideas as to the Elements.—In his original paper (81) announcing his System, Meyer spoke of the elements as follows:

"That the until now undecomposed chemical elements are absolutely undecomposable is, at present at least, very improbable. Rather it seems that the atoms of the weights are not the ultimate but the proximate constituents of the molecules, as well, of the elements as of their compounds. The molecules are to be regarded as particles of a first order, the atoms as such of a second order which again consist of particles of a third higher order.

"The nature of these components of the atoms was sought for shortly after the general acceptance of Dalton's atomic theory, see Prout's hypothesis."

series of articles was contributed by Groshans (94) upon this subject. They dealt mainly with the formulas and physical properties of the compounds of carbon. From the consideration of these, he arrived at the conclusion that carbon, hydrogen and oxygen are simple bodies or true elements; that chlorine is a compound body, consisting of four atoms of simple unknown bodies; so too bromine is a compound body consisting of nine atoms.

His work is criticized and the conclusions refuted by Mendeléeff (99).

104. Other Authors during this Period.—It is unnecessary to quote from the work of Knowles (92) and of Ludwig as they have little bearing here.

Blomstrand's (78, 79) effort to rehabilitate the dualistic and electro-chemical theories of Berzelius was a very earnest and faithful one but met with no success. His division of the elements into the hydrogen-group and the oxygen-group may be mentioned.





## CHAPTER VI.

THE DEVELOPMENT OF THE NATURAL LAW.

1880-1885.

As soon as the Periodic Law had come to be recognized as a discovery of importance, the question as to who should rightly be considered its discoverer became also a matter of moment. The claims of both Mendeléeff and Meyer were urged by themselves and their friends. This discussion will not be entered into here. The Royal Society of England gracefully and justly solved the question by awarding in 1882 the Davy medals to both Mendeléeff and Meyer as the independent discoverers of the Law.

The Royal Society met with some criticism because, by this action, it overlooked and ignored the claims of Newlands. It must be said that, though unquestionably a forerunner in the discovery, little was known of his claims at that time. Victor Meyer (142) in a summary of Prout's hypothesis and the periodic system makes no mention of Newlands.

105. Revival of Prout's Hypothesis.—Attention was again drawn to Prout's Hypothesis in its original form by Mallet's (114) masterly revision of the atomic weight of aluminium and his appended remarks, and by Dumas' discovery (106 $\frac{1}{2}$ ) of an error in the work of Stas. This was his overlooking the absorption of oxygen by melted silver.

Stas' work centered around the determination of the silver-hydrogen ratio and this implied a correction in many of his results which, at least, opened up the question once more as to whether they were integral multiples.

106. Meyer aud Seubert's Review of Dumas' Work.

—These authors (146) after careful critical examination of Dumas' and Stas' work came to the following conclusions:

"The atomic weight of silver, as well as the atomic weights of numerous other elements, all contradict Prout's hypothesis in its characteristic original conception. It must, therefore, be looked upon as having been disproved by experiment. In its new forms it has likewise been disproved, so far as this is possible in the present state of our knowledge. Beyond this it amounts merely to philosophical speculation concerning an idea whose propable correctness will be denied by no one—the Unity of Matter."

107. Mallet's Views Regarding the Hypothesis of Prout.—At the conclusion of his work (114) upon the atomic weight of aluminium this author observed:

"It is interesting to observe that this result also adds one to the cases already on record of the numbers representing carefully determined atomic weights approaching closely to integers, and leads to a word on the reconsideration of "Prout's Law." The recent researches of Mr. Lockyer, not unsupported by evidence drawn from other sources, have tended to suggest the possibility, at least, that the forms of matter which, as known to us under ordinary conditions, we call elements, may be susceptible of progressive dissociation at enormously

high temperatures, and, under circumstances in which this supposed state of dissociation admits of being spectroscopically observed, some of the characteristic features in the spectrum of what is usually known to us as hydrogen become in a very remarkable degree prominent. If such dissociation may really occur, and if the atoms of hydrogen may, as commonly known to us, form either the last term, or any term not far removed in simplicity from the last, in the progressive breaking up of other forms of matter, it is obvious that "Prout's law", or some modification of it, such as was many years ago suggested by Dumas, must be true, the atomic weights of all the other so-called elements must be multiples of that of hydrogen or multiples of that fraction of the hydrogen atom which may result from the dissociation of this body itself. If such fraction be very small as compared with the effect of the inevitable errors of experiment, the experimental vertification or refutation of the law will prove impossible, but if it be considerable, as, for instance, onehalf of the commonly known hydrogen atom, or onefourth as assumed by Dumas, the question admits of practical examination."

The author further questioned the justice of the view taken by Stas of his results that 'Prout's law' is disproved by them or is not supported by them. "The careful work of Stas and others only proves by close agreement of the results that fortuitous errors have been reduced within narrow limits. It does not prove that all sources of constant error have been avoided and indeed this can never be absolutely proved, as we never can be

sure that our knowledge of the substances we are dealing with is complete."

He added that, of course, one distinct exception to the assumed law would disprove it, if that exception were itself fully proved, but this is not the case.

"Out of the eighteen best known atomic weights ten approximate to integers within a range of variation less than one-tenth of a unit. The degree of probability that this is purely accidental is found to be only equal to 1:1097.8. This seems to illustrate the point that not only is Prout's law not as yet absolutely over-turned, but that a heavy and increasing weight of probability in its favor, or in favor of some modification of it, exists and demands consideration."

108. The Views of Clarke.—In his Recalculation of the Atomic Weights (123), Clarke discussed the views expressed by Mallet.

He said that when O=16 is taken as the standard, forty out of sixty-six elements whose atomic weights have been recalculated by him fell within the limit of variation, i.e., one-tenth of a unit variation from whole numbers, and twenty-six fell without. These he examined in detail and concluded that none of the seeming exceptions are inexplicable. Some of them, indeed, carefully investigated, support it strongly. In short, admitting half multiples as legitimate, it is more probable that the few apparent exceptions are due to undetected constant errors, than that the great number of close agreements should be merely accidental. "I began this recalculation of the atomic weights with a strong prejudice

against Prout's hypothesis but the facts as they come before me have forced me to give it a very respectful consideration. All chemists must at least admit that the strife over it is not yet ended, and that its opponents cannot therefore claim a perfect victory."

100. Crookes upon Prout's Hypothesis:-In his address before the British Association (156) he said: "But if the evidence in favor of Prout's hypothesis in its original guise is deemed insufficient, may not Mr. Clarke's suggestion of half multiples place it upon an entirely new basis? Suppose that the unit of the scale, the body whose atomic weight, if multiplied by a series of whole numbers, gives the atomic weights of the remaining elements, is not hydrogen but some element of still lower atomic weight? We are here at once reminded of helium, an element purely hypothetical as far as our earth is concerned, but supposed by many authorities, on the faith of spectroscopic observations, to exist in the sun and other stellar bodies. Most solar explosions present merely the characteristic lines of hydrogen, C, F, and H, and along with them one particular line which at first was classed in the group, but which is a little more refrangible and is designated by the symbol Dz. According to Mr. Norman Lockyer and the late Father Secebi, this ray undergoes modifications not comparable to those affecting other rays of the atmosphere. In the corresponding region of the spectrum no dark ray has been observed. That the accompanying lines C, F and H pertain to hydrogen is evident; and as Dz has never been obtained in any other spectrum it is supposed to

belong to a body foreign to our earth, though existing in abundance in the atmosphere of the sun. To this hypothetical body the name helium is assigned. In an able memoir on this subject read before the Academy of Brussels, the Abbé E. Speé shows that, if helium exists, it enjoys two very remarkable properties. Its spectrum consists of a single ray, and its vapor possesses no absorbent power. The simple single ray, though I believe unexampled, is by no means an impossible phenomenon, and indicates a remarkable simplicity of molecular constitution. The non-absorbent property of its vapor seems to be a serious objection to a general physical law. Professor Tyndall has demonstrated that the absorptive power increases with the complexity of molecular structure, and hence he draws the conclusion that the simpler the molecule the feebler the absorption. This conclusion the Abbé Speé regards as perfectly legitimate: but it neither explains nor even necessitates the absence of all absorptive power.

"Granting that helium exists, all analogy points to its atomic weight being below that of hydrogen. Here, then, we may have the very element, with atomic weight half that of hydrogen, regarded by Mr. Clarke as the basis of Prout's Law."

These speculations read very strangely in the light of our later knowledge of helium.

110. Meyer and Seubert on Prout's Hypothesis.—The authors (147) admit that in Prout's Hypothesis there may be a kernel of truth concealed but maintain still that in its present form it is untenable.

Wherever it has been put to the proof by accurate determination it has been shown that these atomic weights are not exact integers or multiples and this is independent of the ratio of oxygen to hydrogen.

The authors note that the atomic weights of more than the fourth part of all elements are nearly exact multiples of the half-atom or the equivalent of oxygen. Such regularities are worthy of note but to rectify the atomic weights by means of them would be as inadmissable as the rounding of fractions into whole numbers.

III. Groshans on Prout's Hypothesis.—Groshans considered (188) this hypothesis with special reference to the atomic weights of carbon and oxygen.

The author showed that isomeric organic compounds, containing carbon, hydrogen and oxygen, which have the same molecular weight but different composition, belong to one of seven general series, the molecular weights in each of which are given by 14n + 2x where x is any unit less then seven. He argued from the equality in the molecular weights of such compounds of different composition, that the atomic weights differed by some multiple of that of hydrogen, so that C + 4 = 0 and 4C = 03 and hence that C = 12 and O = 16.

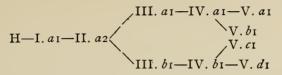
between the Atomic Weights and the Other Properties of the Elements.—In a communication to the Philosophical Magazine in 1882, Thomas B. Bayley (124) tried to show the connection between the atomic weights and the properties of the elements. He followed the arrange-

ment in the order of the atomic weights and took note

ment in the order of the atomic weights and took note of the periodic recurrence of the same group of properties in sets of seven. He distinguished between the degree of relationship in the various groups and families and divided the elements into cycles, series and individuals. A reference to his table will give an idea of the plan of his arrangement.

I. 
$$a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$$
 III.  $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$  III.  $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$  III.  $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$  IV.  $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \end{cases}$   $a \begin{cases} 1 \\ 2 \\ 3 \end{cases}$   $a \begin{cases} 1 \\ 3 \end{cases}$   $a \begin{cases} 1 \\ 4 \end{cases}$   $a \end{cases}$   $a \begin{cases} 1 \\ 4 \end{cases}$   $a \rbrace$   $a \rbrace$ 

The main family of all the groups is I.ai; III.ai; III.ai; IV.ai; V.ai; and with this the groups are connected as follows:



By this method each element, whether known or unknown, is represented by a symbol expressing its position with regard to the other elements and its relation to these, whether axial, as among the members of a family, or lateral, as between adjacent elements in a series or cycle. The following circumstances are connected with the properties of an element.

- a. The position or sequence in a series.
- b. The proper position in the series.
- c. The position in a cycle.

Bayley also gave, in a diagram like that of Meyer, the curves obtained by taking the atomic weights as ordinates and plotting out the atomic volumes and other properties as abscissae. His diagram with the elements filled in at their proper places is reproduced, in connection with an article of Carnelley.

113. Gladstone's Address before the British Association.—The question as to the possibly composite nature of the chemical elements was taken up by Gladstone, at the meeting of the British Association in 1882. He first gave (131) a very interesting account of the various ideas and theories as to the primal elements held by the different ancient peoples and alchemists.

The question as to whether the elements known to the chemist at present are to be considered simple undecom-

posable bodies or not, he approached from three "points of attack."

I. The spectroscope. It was hoped that by finding identical rays in spectra of different elements a common constituent might be proved to be present. A certain similarity has been observed but not identity. This is negative but not fatal to the idea that the elements are compounds for it is known that the spectrum of a compound is not made up of the spectra of its components.

Again the multiplicity of rays given out by some elements might point to a complex constitution. Still this may be merely complexity of arrangement. Lastly, spectroscopic work upon the sun has shown some remarkable phenomena. The explanation of these, however, is not clear as yet.

- II. The composite nature of the elements might be inferred from certain peculiar regularities in the atomic weights. Here Gladstone discussed the work of Dumas, Newlands and Mendeléeff.
- III. From specific refraction. Here we find that light is acted upon very differently by these groups of elements and by the compound radicals and the organic homologous series of hydrocarbons. The elementary radicals, if they are such, are essentially different from the compound radicals though their chemical functions are similar.
- "The remarkable relations between the atomic weights of the elements and many pecularities of their grouping, force upon us the conviction that they are not separate

bodies created without reference to one another, but that they have been originally fashioned, or have been built up from one another, according to some general plan."

114. Hartley on Spectroscopic Evidence as to the Nature of the Elements.—With regard to the evidence to be gotten from the spectroscope, Hartley (128, 129) wrote: "There is evidently a harmonic relation between the lines in the spectra of magnesium, zinc, cadmium, aluminium and in those of calcium, strontium and barium, when two octaves of the spectrum are examined. This extension to two octaves is possible by means of photographs. The fundamental vibrations appear to be all in the infra-red region.

"In order that harmonic relations between lines and groups of lines may be rendered apparent it is necessary to map spectra according to their oscillation frequencies instead of wave lengths."

The author has thus mapped the wave frequencies in one mm. of the chief rays in the spectra of Mg, Zu, Cd, Cu, Ag, Si, B, and Al. The data thus obtained support the view that elements whose atomic weights differ by a constant quantity and whose chemical character is similar, are truly homologous or in other words are the same kind of matter in different states of condensation.

115. Hartley's Criticism of Lockyer.—Hartley also criticized the work of Lockyer: "It will be remembered that Mr. Norman Lockyer has proposed to explain the occurrence of several coincident lines in the spectra of different elements by supposing that each spectrum is

composed of several spectra, and that these compound spectra are the spectra of compound bodies and not of elements. The action of a low temperature causes the vibration of a compound molecule, while the action of a high temperature causes a breaking up of the molecule either into smaller molecules of the same element, or into those of distinct elements. It appears also from the way in which he has treated the subject, that every elementary substance may be decomposed into as many simple substances as there are rays in its spectrum. I allude here to the observations concerning the lines in the spectra of iron, calcium, magnesium, lithium, and hydrogen. M. Lecoq de Boisbaudran, also Vogel and Van Monckhoven<sup>3</sup> have disposed of some of these facts upon which this theory is founded. With even very moderate dispersive power, something like 1200 lines can be recognized in the spectrum of iron, an element which has an atomic weight of 56, and it is simply inconceivable that a body of the chemical nature of iron can have a molecular structure so complex as to be composed of 1200 different simpler substances. Mr. Lockyer's hypothesis seems quite incompatible with the theory that the spectra are composed with harmonic vibrations, because a compound body would give two or more series of harmonics related to two or more fundamental vibrations, and elements having a common component should give spectra in which the same series or groups of lines should appear. If, therefore, we are to draw inferences

<sup>1</sup> Compt. rend., 73, 943, and 82, 1264.

<sup>&</sup>lt;sup>2</sup> Ber., 13, 274.

<sup>3</sup> Compt. Rend., **90**, 520,

as to the compound nature of substances from coincident lines in their spectra, it is not single lines but harmonic series that we must look to for coincidences.

"It is upon there currence of such groups of lines that Ciamician (118) has based his conclusion that silicon is composed of carbon and oxygen, with a corresponding weight 12, 16, 28, and aluminium, of boron and oxygen, 11, 16, 27."

116. The Numerical Relations of Fedaroff.—Fedaroff (127) has discovered a somewhat obscure and yet singular relation between the atomic weights. He gives a table in which the elements are placed in an ascending series with a uniform difference of 0.5. This table follows on p. 164.

If the numbers in these tables be raised to the power  $\frac{3}{2}$  and the result be multiplied by  $\frac{7}{8}$  one will obtain approximately the atomic weights of the elements. Admitting the homogeniety and similarity of the atoms, one must conclude, according to the author, that the elements are arranged in the natural system in arithmetical progression increasing with the surface of their atoms. In Group VIII., for example, the ratio of the atomic surfaces are as 4, 6, 9, whilst the surfaces of Cl, Br, and I are as 3, 5, 7. The atomicity and general chemical properties of the elements are essential functions of these surfaces.

117. Laurie on the Physical Properties.—Laurie (132) has been a valuable investigator in the direction of the extension of the Periodic Law along the lines of the physical properties. One of his more important pa-

THE TABLE OF FEDAROFF.

|          | 8.5         | :       | { 16.5                     | :      |          | C-+-2            | :      | :            | 36.5            |             |
|----------|-------------|---------|----------------------------|--------|----------|------------------|--------|--------------|-----------------|-------------|
| VIII.    | 7.5 ? 8.0 ? | :       | Cr 15.0 Mn15.5 Fe16.0 Ni { | :      | for a Dd | Rh \ 24.0 1 u 24 | :      | 32.0         | Os 36.0 Ir 36.5 |             |
|          | ۸.          | ٠       | He 1                       | •      | Ru       | Rh               | ٠      | ۸.           | Os              | ۸.          |
| VII.     | 7.5         | 12.0    | 1 15.5                     | 20.0   | 23.5     | 28.0             | 31.5   | 35.5         | 40.0            | 43.0 ?      |
| Δ        | ĭ           | $\Box$  | Mr                         | Br     | ۸.       |                  | ۸.     | ٠.           | ٠.              | ۸.          |
| VI.      | 7.0         | 11.5    | 15.0                       | 19.5   | 23.0     | 27.5             | 31.0   | W 35.0       | 39.5            | 43.0        |
|          | 0           | S       | Ç                          | S1     | Mo       | Te               | ۰.     | $\mathbb{A}$ | ۸.              | ۸.          |
| V.       | 6.5         | 0.11    | V 14.5                     | 0.61   | 322.5    | 0.72             | 30.5   | 1 34.5       | Bi 39.0         | 42.5        |
|          | Z           | Д       | >                          | As     | Z        | S                | ۸.     | Ta           | Bi              | ۸.          |
| IV.      | C 6.0       | Si 10.5 | Ti 14.0                    | ? 18.5 | Zr 22.0  | Sn 26.5          | ? 30.0 | ? 34.0       | $\rm Pb38.5$    | Th 42.0     |
| III.     | B 5.5       | 1 10.0  | 13.5                       | a18.0  | 21.5     | 1 26.0           | 29.5   | ? 33.5       | Tl 38.0         | ? 41.5      |
| 11       |             |         |                            |        |          |                  |        |              |                 |             |
| ن ا      | Be 5.0      | 9.5     | 13.0                       | 17.5   | 21.0     | 25.5             | 29.I   | ? 33.0       | 37.5            | 41.0        |
| II.      | Be          | Mg      | Ca                         | Zn     | Sr       | Cd               | Ba     | ۸.           | Hg37.5          | ۸.          |
| Group I. | 4.5         | 0.6     | 12.5 Ca 13.0               | 0.71   | 20.5     | 25.0             | 28.5   | 32.5         | 37.0            | 40.5 ? 41.0 |
| Gro      | r:          | Na      | M                          | Cu     | Rb       | Ag               | Cs     | ۸.           | Au Pt           | ۸.          |

pers was upon the relations between the heats of combination of the elements and their atomic weights.

—Gerber's Modification of the Hypothesis of Prout. —Gerber (133) has so modified the Proutian hypothesis that a discussion of it comes quite properly under the heading of the general numerical relations. According to him all the atomic weights are simple multiples of one of the four following numbers:  $d_1 = 0.769$ ;  $d_2 = 1.995$ ;  $d_3 = 1.559$ ;  $d_4 = 1.245$ . The monatomic elements are multiples of  $d_1$ ; the tetratomic, the alkaline earths, and the elements related to C and O are multiples  $d_2$ ; the triatomic and pentatomic of  $d_3$ ; and the metals, in a narrower sense, of  $d_4$ . Between these four numbers the fol-

Weights.—Mills (137) in a discussion of the melting and boiling points as related to chemical composition showed that the atomic weights may all be expressed by the equation

lowing relation can be seen:  $d_1:d_2:d_3:d_4::\frac{10}{13}:2:(\frac{5}{4})^2:\frac{5}{4}$ .

$$y = px - n \left(\frac{n}{n+1}\right)$$
.

Where n = 15; p = periodic or group number and x is an ordinal integer. From this formula he calculated the atomic weights and found a close correspondence with the observed numbers. The author then discussed the genesis of the elements on a theory of gradual cooling, using the analogy of iodine; sulphur; phosphorus and its allotrophic form; NO and  $N_2O_2$  etc.

He further gave a classification of the elements, de-

fining an element as one of a list of complex simple substances whose numerics are of the form y=(1.2.3...) 15—15 (.9375). A table is given based on this. He regarded As, Sb, probably Er and perhaps Os as the only known polymers of primitive matter.

His method of tabulation made it possible for the number of the elements to be infinite but the methods of discovery are not infinite and he thought few more would be discovered unless by a new method or a new combination of methods.

120. Carnelley's Study of the Relations of Physical Properties.—Carnelley, who has done much to extend the Periodic Law, and was singled out above all others by Mendeléeff as having aided in its development, published in 1884 a paper (138) in which he considered especially the melting and boiling points and the heats of formation. First he examined these properties for the halogens and established for them the correctness of the Periodic Law. From this he went further to the calculation of unknown melting and boiling points and then showed how the knowledge of these properties would enable one to determine the atomic weight of an element, and could in fact be used in the place of the vapor density and the specific heat when these failed to give satisfactory results. The position of an element in the table could also be determined by the use of the same properties. Many tables and a diagram accompany the article.

121. The New Law of Groshans,—Groshans (141) announced in 1882 what he called the New Law:

"The specific weights of bodies measured at the temperature of the boiling point or any corresponding temperatures, are proportional to their density numbers. Each element has a density number. Thus for C, H, and O it is 1, for S it is 2, for N, 3, etc."

In a later paper (144) the author made use of this law to bring out the connection between the specific gravities and the atomic weight periods.

122. Pelopidas Compares the Elements with the Organic Radicals.—Pelopidas (134) showed in 1883 that, as the elements are ordered by rising atomic weights in the periodic system, so the hydrocarbon radicals and the nitrogenous organic radicals can be arranged in definite series, in periods, in accordance with their composition. In these periods is to be seen also a repetition and a gradual transition of properties of the individual members of a period. Also the number of members or of radicals of each period is just as large as that of the elements in a period of the natural system. Thus, for instance, in the compound ammonium or alcohol radicals  $C_nH_{2n+1}$  a transition to acid radicals is found.

If one places in the first group with Na the alcoholic tetra-ammonium radical  $N(C_nH_{2n+1})_4$  or  $N(C_mH_{2m+4})_4$  and derives the remaining groups by a gradual reduction of the amount of hydrogen, one gets in the seventh group a radical of the composition  $NC_mH_{2m-2}$  whose representative would be cyanogen which is a genuine analogue of C1 and F. The following example is also given:

I.  $C_nH_{2n+1}$ . II.  $C_nH_{2n}$ . III.  $C_nH_{2n-2}$ . IV.  $C_nH_{2n-2}$ . V.  $C_nH_{2n-3}$ . VI.  $C_nH_{2n-4}$ . VII.  $C_nH_{2n-5}$ . VIII.  $C_nH_{2n-6}$ .

According to this one returns at the end of the groups to the first group radical or  $C_nH_{2n-7}$ , or the benzene radical. If alcoholic radicals are the first members of the series then acid radicals are the last and these, like the corresponding elements, are in position to form higher oxidation steps. Thus, for instance, the radical of the sixth group will give an hydroxide  $RH_2O_4$  or  $C_nH_{2n-4}$ ,  $H_2O_4$  or  $C_nH_{2n-2}O_4$ . This formula can only be looked upon as an expression for the composition of the homologues of oxalic acid.

- gave in 1884 a diagram to illustrate the Periodic Law. He made use of the spiral, as had already been done by Baumhauer and in a measure by Hinrichs. The spiral was constructed as follows. From a common centre seven radii diverge and on these are placed the atomic weights beginning with the least. Thus all of the elements of one group will fall upon the same radius. Lithium is placed on the first radius at a distance of seven mm. then follows Be on the next at a distance of nine mm. Sometimes, as for Fe, Co, and Ni, instead of one element several are placed on the same line at once.
- 2. In each line, or family, two distinct groups of elements may be distinguished by taking alternate elements beginning with the second or third member. The beginning members of each family have a special position peculiar to them and also an intermediate position between the chief groups.
- 3. The distance between the members of every group is subject to a distinct periodicity, thus;

Lithium family. 16–16–24–22–23–25–63. Beryllium family. 15–16–28–22–25–25–63.

So too we have the differences in the O and N families:

Oxygen family. 16-21-25-18-29-59-56.

Nitrogen family. 17-20-26-19-28-60-?.

- 4. The table is intended also to show valence and chemical behavior as functions of the atomic weights.
- 5. The specific gravities stand in a peculiar relation to the atomic weights.
- 6. Related groups of elements seem to possess homologous spectra; other properties are also mentioned.
- 124. Berthelot's Ideas as to Primal Matter.—Berthelot (145) gave in "Les Origines de l'Alchimie," after his criticism of the periodic system of Mendeléeff, his own ideas as to the constitution of matter and the primal matter. La critique est facile mais l'art est difficile.
- "The fundamental identity of the matter contained in the chemical elements and the possibilities of transmutation among these reputed simple bodies may be admitted as very plausible hypotheses without the existence of a unique form of matter, capable of isolation, resulting from them. One of these hypotheses does not carry the other as necessary sequence although this has been the view held up to the present. This merits particular attention.

"In truth, in admitting the unity of matter as established it is conceived that the matter is one susceptible of a certain number of states of stable equilibrium, beyond which it will not be manifested. The sum of these stable states will form the simple bodies known to-

day and the simple bodies which will be discovered one day and even formed synthetically, supposing that one should ever attain to the discovery of the law of generation. But one has always reasoned by comparing these multiple states of equilibrium of that matter with the actual compounds formed by the addition of simpler elements.

"Still these matters can be thought of in an entirely different manner. It is possible that the diverse states of equilibrium in which the fundamental matter manifests itself are neither buildings made up by the addition of different elements, nor buildings made up by the addition of identical elements but unequally condensed. a word, it does not appear necessary that all these molecular buildings should represent the entire multiples of a small number of ponderable elementary units. can just as well fancy that such edifices offer, the one by correspondence with the other, the generating relations of another order: such, for instance, as the relations existing between the geometric symbols of the different roots of an equation, or more generally between the multiple values of one function defined by mathematical analysis. The fundamental matter would represent then the generating function and the simple bodies would be the determined values. \* \* \*

"According to this hypothesis, a reputed simple body can be destroyed but not decomposed in the ordinary sense of the term. At the moment of its destruction the simple body is instantaneously transformed into one or more other simple bodies, identical or analogous to actual elements. But the atomic weight of the new elements could not show a commensurable relation to the atomic weight of the primitive body which will be produced by its metamorphosis.

"According to this view, the body which would result by the metamorphosis of any one of the elements ought not to be regarded as a simple body by comparison with it.

"The different simple bodies can be made up of the one matter distinguished only by the nature of its motions. The transmutation of an element will not then be anything more than the transformation of the movements which correspond to the existence of that element and which communicate to it its peculiar properties, in these specific movements corresponding to the existence of another element." Berthelot says that these speculations were presented before the Société Chimique de Paris in 1863.

of the Elements.—The author began his paper (140) by commenting upon the work of Gladstone. "Gladstone (Phil. Mag. (5) IV p. 379.) has proposed to account for the occurence of elements as to degree of distribution.

"Gladstone divides them into(1) plentiful, (2) common, (3) rare, (4) very rare, and shows that the average vapor densities of the first class are less than the second, the second than the third, etc., concluding that elements having least vapor densities tended to remain more towards the surface during the period of the earth's formation, whilst elements having a high vapor-density accumulated more

toward the center and hence occur butrarely on the surface." He then referred to the fact that Mendeléeff has shown that elements with small atomic weights are the most abundant. He considered then in connection with the Mendeléeff table:

- r. Reducibility of the elements, (elements belonging to the odd series more easily reducible):
  - 2. Occurence in the free state:
  - 3. Ocurrence in the compound state:

He then expressed the facts in terms of Lothar Meyer's curve of the elements.

Carnelley's paper (150) read before the Aberdeen meeting of the British Association in 1885, suggesting a cause for the periodic law, used chiefly analogies drawn from organic chemistry. As we have seen, these analogies have been frequently called into aid before in solving this problem and we will come upon a number of other papers based upon them.

Carnelley argued the compound nature of the elements from the analogy to the hydrocarbons or alcohol radicals. He summed up his previous work.

- 1. His first paper dealt with a comparison of the melting and boiling points and heats of formation of the normal halogen compounds of the elements and it was shown that relationships existed between them, depending upon the atomic weight of both the positive element and the halogen.
- 2. The second paper dealt in a similar manner with some of the physical properties of the normal alkyl

compounds of the elements and the same relationships were observed.

3. The third paper showed that normal halogen and normal alkyl compounds of the hydrocarbon radicals exhibit, with one exception, relationships similar to those of the corresponding compounds of the elements. From these he inferred:

"That the elements, as a whole, are analogous to the hydrocarbon radicals, having a similar function in their several compounds and most probably a somewhat similar chemical constitution or they are analogous in both form and function."

A very full and exhaustive comparison was given in tables and in diagrammatic curves to illustrate and prove the above assumption. He gave two large diagrams showing the division of elements and hydrocarbons into groups and also their evolution.

In his general conclusions, he drew the further inference: "That the elements are not elements in the strict sense of the term, but are in fact compound radicals, made up of at least two simple elements, A and B." A system of elements built up in this way should fulfill the following conditions.

- 1. They must be capable of division into series and groups, that is to say, they must exhibit periodicity.
  - 2. The several series must run in octaves.
- 3. Some feature corresponding to "odd and even series" must be exhibited.
  - 4. The atomic weights must increase across the sys-

tem from the first to the seventh group, from the positive to the negative end of each series.

- 5. The atomicity must increase from the first to the fourth, or middle group, and then either increase or diminish to the seventh.
- 6. It should exhibit some feature corresponding to the eighth group in Mendeléeff's table of the elements.
- 7. The atomic weights in such a system should coincide with or approximate to the commonly received atomic weights of the elements. The table which he appended does not rigorously accord with all these conditions. Indeed it could hardly be expected that it would since he insisted on copying the defects of Mendeléeff's table as well as its more valuable features. He made use of Bayley's table slightly modified. The table requires the assumption of an element of negative atomic weight, namely B = -2. There is a difference between the observed and calculated weights, though not a very large one. All of the weights are even numbers which of course makes a very striking variation from the actual weights of the elements. He omitted a few elements such as Ag, Au and Fe since their proper places are not well known.

As to the structure of the system:

First. The binary elements (except Ti, V, Cr, and Mn) which would be represented by the formula  $A_nB_{2n} + (4-x)$  may all be represented by the general formula  $A_nB_{2n} + (2-x)$ , in which A = 12 and B = 2, whilst x = mth group + nth homologous series to which any element belongs. A is supposed to be a tetrad element identical with carbon, and B a monad element.

|  |                   |               |                |           |            |                      | I          |          |                   |                  |                    |          |           |          |            |
|--|-------------------|---------------|----------------|-----------|------------|----------------------|------------|----------|-------------------|------------------|--------------------|----------|-----------|----------|------------|
|  |                   |               |                | ,         | /          | /                    |            | 1        | <u></u>           |                  |                    |          |           |          |            |
|  |                   |               |                | A 19      | 0 16       | /N 14.0              | -C /2.0    | B 109    | /Be 91            | رك 70            |                    |          |           |          |            |
|  |                   |               |                | 164       | /6         | 7, 0                 | %          | 16.1     | 149               | /6<br>/6         | ,                  |          |           |          |            |
|  |                   |               |                |           | S          | ٦                    | Sı         |          |                   |                  |                    |          |           |          |            |
|  |                   |               |                | Cl 35.4   | 5 32 0     | P 310                | Sı 280     | Al 27.0  | Mg 240            | Na 23.0          |                    | DIE      |           |          |            |
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| _   |                                |   | (An B2n-4)1V   | (An Ban-s) V GROUP V           | (An Ben-6)VI                                   | (An Ban-7)VII   |           | ^-              |           |                |                        |                 | (An B2n-4)1V                              | V (An B2n. 5) 117-V                                     | 11. (AnBan-6)0vi                             | 11 (An Bn-1)1.vIII                        |
| GENERAL FORMULA<br>10 (A B) I                 | 4 B, 232 (A, B, n) D           | AB, 170 SO AB 234 (An Ban,) III         | AB 180 JE AB 236 (An Ben. 2) II [(An Ben. 4) IV GROUP IV B | AB, 182 SE AB 238 (An Ban-3) I | AB104 JE AB240 (AB2n.4) TI (An Ban-6) MI GROWN | 4B188 36 AB242 (AB2n.5) VIII (Andan-7) VIII GROUPVIII |           |                 |           | (A,B, 2,, 7) 1 | $(A_{a}B_{2n-6})_{11}$ | $(A, B_{2n-9})$ | (A, B2n-10) IV [AnB2n-4) IV] GROUPXII > b | (A, B, n, ) 111-v (A, B, s, s) 111-v (A, B, s, s) 111-v | (An B2n-12) 11-VI- (An B2n-6) 5-VI GROW-OXIV | (An B2n-13) IVII (An En-1) IVIII GROUP XV |
| G<br>AB 230                                   | A B 232                        | AB,234                                  | AB 236   | AB 238                         | AB 240   | AB 242  | ı         | ı               | ı         | ı              | ı                      | į               | 1   | 1   | 1  | 1   |
| GENERAL FO<br>"33" 4" (".18") 56 33,530 (A.B) | AB 176 56                      | AB,178 56                               | AB 180 56  |                                |  | AB 186 56   | AB 192    | AB 194          | AB 198    | AB 198         | AB 200                 | AB 202          | AB 204(208)                               | AB 206(210)   | AB 208                                       | AB 210                                    |
| 2   | 3                              | 04                                      | ,3   | 0,4                            | 0,5  | 9   |           |                 |           | 07             | 9                      | 0.7             | 3   | 04  | 07   | 3   |
| AB 134  | AB 136                         | AB 138                                  | AB 140   | AB, 142                        | AB 144   | AB 146  | ı         | 1               | 1         | AB 158         | AB 160                 | AB 162          |   | AB 174  | AB 176                                       | AB 178                                    |
| 87  | 84                             | 8,7                                     | 87.  | 93                             | 84   | 84  |           |                 |           | 84             | 84                     | 84              | 8,4                                       | 8# (  | 9,4  | 46  |
| AB 86   | AB 88                          | AB 30                                   | AB 32  | AB, 34                         | AB, 96   | A,B, 38   | A, B, 104 | A., B., 106     | A, B, 108 | A.B. 110       | A,B, 112               | AB 114          | AB 116(120) 48 AB 164                     | AB 126(122) 48 AB 174 40 AB 206(2:0)                    | AB 128(24) 48 AB 176 40 AB 208               | AB, 130 (126) 48 AB, 178 40 AB 210        |
| 80  | 87                             | 8,4                                     | 3  | <b>*</b>                       | 3  | 3   | 8         | 48              | 48        | 8*             | 4/8                    | 84              | 84  | 8   | 4.8  | 4,9                                       |
| A & 36  | AB 40                          | Ag 42                                   | AB 48  | AB So                          | AB, 22   | A,B, 54   | AB Se     | AB 58           | AB 60     | \49 62         | \AB 64                 | \AB 66          | AB 68(72)                                 | 1 AB 78(74) 48  | 1 A & 80(76) 48                              | 146, 8208) 48                             |
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| ~   | (3-1)                          | ,                                       | , _  |                                | >>   | $\approx$   | $\approx$ | $\approx$       | $\approx$ | $\leq$         | 48                     | 48(4            | 48(4                                      | .,  |  |   |
|   | 4 - AnB.                       | K. GROUP<br>B2                          |  |                                | A,B, 22 (                                      | AB 24   | AB, 26    | AB, 28          | AB 30     | AB 32          | A,B, 34                |                 | D=20                                      |   |  |   |
|   | SMUL.                          | 300                                     |  |                                | 9/   | 9/  | 9/        | 91              | 91        | 91             | 9/                     |                 | *   |   |  |   |
|   | GENERAL FORMULA - An Bu+ (2-1) | N = SEKIES K. GRO<br>A = 12 ANO B = - 2 |  |                                | AB 6   | / AB 8  | AB,10     | AB, 12          | *   Y     | \AB 16         | \AB3,18 16             |                 | A=DB₊                                     |   |  |   |
|   | GEN                            |   |  |                                |  |   |           | *               |           |                |                        |                 |   |   |  |   |

Second. The atomic weights are all even integers. This is due to the value of B which has been for the sake of simplicity taken as equal to—2 whereas its value should lie between—1.99 and—2.0.

Third. The difference between odd and even series is here the difference between saturated and unsaturated binary elements.

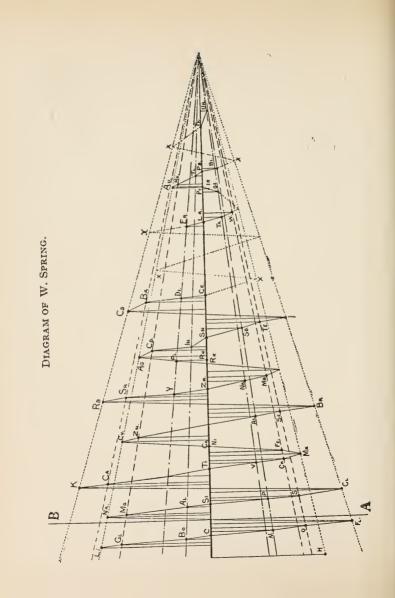
Fourth. The difficulty seen in subtracting the atomic weight of a negative element as B from positive A could be obviated by substituting  $DB_4$  for A where D is a heptavalent element of the atomic weight 20.

Fifth. This system would admit of isomeric elements.

Sixth. The elements are all, except hydrogen, supposed to be composed of two simpler elements, viz, A=12 and B=-2. Of these A is identical with the element carbon whilst B is a substance of negative weight possibly the ethereal fluid of space.

"If the theory be true, then it is interesting to observe that whereas the hydrocarbons are compounds of carbon and hydrogen, the chemical elements would be compounds of carbon with ether (atomic weight equal to —2), the two sets of bodies being generated in an exactly analogous manner from their respective elements. There would hence be the primitive elements carbon, hydrogen and ether. Two tables are given showing this generation of the elements.

127. Spring's Diagram of the Elements.—In 1881, Professor W. Spring, (119), of the University of Liege, prepared a diagram of the elements for the use of his



students. This was reproduced in the form of a large lithograph, without accompanying notes. It resembles the diagram of Gibbs and is the precursor of those of Reynolds and Crookes. It is given on page 178.



## CHAPTER VII.

THE DEVELOPMENT OF THE NATURAL LAW. 1885–1890.

It is impossible to give any general characterization of this period. The work included in it is of very varying degrees of importance and interest and is not along any special line. We find again numerical relations mentioned, usually of a more abstruse nature than those which have been recorded in the earlier periods.

There is much which shows a trend of thought toward the theory of the unity of matter and the composite character of the elements. The most important papers of the period are those of Reynolds, Crookes, Grünwald, and the Faraday Lecture of Mendeléeff.

128. Rydberg on the Nature of the Periodicity.—Rydberg published in the years 1885 and 1886 two papers, the first upon the periodic system and its graphic representation and the second upon the laws of the atomic weights, in which he attempted to bring out some new relations and to solve the mystery of the connection between these constants.

The author observed in his first paper (151) that while it is generally agreed, from the investigations of Mendeléeff and Meyer, that the properties of the elements are periodic functions of their atomic weights, no attempts so far have been made to determine the nature of these functions. It is necessary to form the curves of these properties as has been done

by Lothar Meyer for the atomic volumes. This curve of Meyer was discussed by Rydberg and curves for the specific gravities, etc., were constructed and conclusions drawn from them. His general conclusions were that these curves show clearly that it is only the atomic weight and nothing else which governs the specific gravities and melting points as well as expansion coefficients, refraction equivalents and in short all the known physical properties of the elements. To state it more explicitly:

- 1. The physical characteristics of the chemical elements are functions of their atomic weights.
- 2. These functions are sums total of a non-periodic and a periodic part.
- 3. The periodic part is the function of a series of single periodic functions with variable amplitude, whose periods are sub-multiples of that of the first one, i. e., are related as a base tone to its harmonic upper tone.

As to the chemical nature of the element, he concluded that two atoms of the same element attract each other with a force, the strength of which is a periodic function of the atomic weight.

- 1. Between atoms of the same element act forces of two different kinds, non-periodic and periodic functions of the atomic weights.
- 2. The non-periodic force seems to increase continuously with the atomic weight and follows, at least for the greater distance, Newton's Law; it is always attractive.
- 3. The periodic variable forces correspond to the terms in the function of the specific gravity and have the same

RVDBERG'S TABLE OF THE ATOMIC WEIGHT DIFFERENCES.

| -  |               |               |               |               |               |               |  |  |  |  |  |
|----|---------------|---------------|---------------|---------------|---------------|---------------|--|--|--|--|--|
|    | II—I.         | III—II.       | IV—III.       | v-iv.         | vi–v.         | vII-vI.       |  |  |  |  |  |
| 2  | Be—Li<br>2.07 | B—Be<br>1.82  | C—B<br>1.07   | N—C<br>2.04   | O—N<br>1.95   | F-O<br>3.10   |  |  |  |  |  |
| 3  | Mg—Na<br>0.94 | Al—Mg<br>3.10 | Si—A1<br>0.96 | P—Si<br>2.96  | S—P<br>1.02   | C1—S<br>3·39  |  |  |  |  |  |
| 4  | Ca—K<br>0.88  | Sc—Ca<br>4.06 | Ti—Sc<br>4.03 | V—Ti<br>3.10  | Cr—V<br>1.35  | Mn—Cr<br>2.35 |  |  |  |  |  |
| 5  | Zn—Cu<br>1.70 | Ga—Zn<br>5.02 | • • • •       | ••••          | Se—As<br>3.97 | Br—Se<br>0.89 |  |  |  |  |  |
| 6  | Sr—Rb<br>2.10 | Y—Sr<br>2.30  | Zr—Y<br>0.80  | Nb—Zr<br>3.30 | Mo—Nb<br>2.20 | ••••          |  |  |  |  |  |
| 7  | Cd—Ag<br>4.04 | In—Cd<br>1.70 | Sn—In<br>3.95 | Sb—In<br>2.25 | Te—Sb<br>5.40 | I— Te<br>1.54 |  |  |  |  |  |
| 8  | Ba—Cs<br>4.16 | La—Ba<br>1.64 |               | ••••          | ••••          | ••••          |  |  |  |  |  |
| 9  | ••••          |               | ••••          | ••••          |               | • • • •       |  |  |  |  |  |
| 10 |               |               | ••••          | ••••          | W—Ta<br>1.60  |               |  |  |  |  |  |
| 11 | Hg—Au<br>3.60 | Tl—Hg<br>3.90 | Pb—T1<br>2.69 | Bi—Pb<br>1.11 | ••••          | ••••          |  |  |  |  |  |
|    |               |               |               |               |               |               |  |  |  |  |  |

periods as those. They are alternately attracting and repelling.

He thought that the proximate cause for a periodicity in the physical properties must be a corresponding periodicity of the force acting between the atoms: and that periodically variable forces acting between the atoms are generated by periodic movements of the latter, by which the surrounding ether is caused to vibrate. The amplitudes of these vibrations are governed by the energy of the atomic movements, which is a periodic

function of the atomic weight, and in their turn govern the strength of the generated force.

The atomic weight differences were also discussed by him and brought into conformity with a periodic law. (See table.) The reasoning used throughout the work is largely mathematical.

A certain amount of periodicity is observable in this table. There are imperfections which would largely obscure the actual degree of regularity to be observed in these atomic weight differences. The table needs no detailed explanation.

129. Relations between the Atomic Weight Differences Observed by Rydberg.—In the second paper (152) the starting point of the examination was the observation that the majority of the smaller atomic weights are nearly whole numbers though they do not absolutely coincide with them. The probability that this is no accident is found sufficient to justify writing the atomic weights in the form N+d where N is a whole number. The differences in the value of N for the first accurately known atomic weights showed on examination that they, with few exceptions, possess the value 4n or 4n + 3. A closer examination revealed that the form 4n + 3 belonged to the elements of odd valence and 4n to those of even. The probability that this was accidental was found to be very small.

In order to find the d values two suppositions were made:

1. That the forms 4n + 3 and 4n respectively hold good for all elements.

2. That the difference p of the N values was constant for two consecutive elements of the same group. According to (1), p must have the form 4n.

The value of p was found constant and equal to 44 by comparing the extreme members of each group. By this the justice of the supposition was placed beyond doubt and the values for N and d perfectly determined. Lastly, the d values of the two series of elements (odd and even valences) were examined separately. They proved to be periodic functions of N (or n.) The length of the period was equal to 44(11); d=x-N where x is the observed atomic weight and N is the calculated one. He concluded that it is impossible to longer regard the elements as simple independent bodies.

It is scarcely necessary to point out the very doubtful character of the d values. Yet the author attached much importance to them. He thought that they point to the atoms being made up of hydrogen atoms and a second periodic constituent (H may possibly be divided itself). This member he said might enclose the kernel of hydrogen atoms as an envelope. He noted the close connection between the curve gotten for these values and the curves for the physical properties of the elements. Tables are given in the original papers containing these curves.

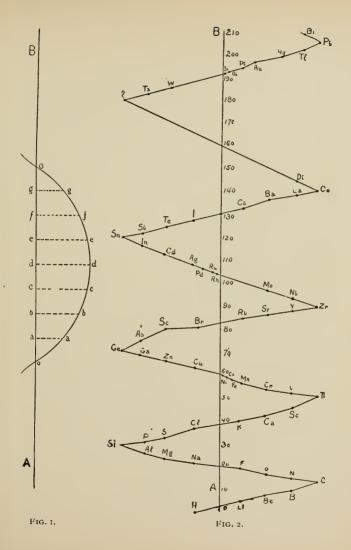
130. Reynold's Diagram Representing the Periodic Law.—In 1886 Reynolds devised a diagrammatic representation of the periodic law (155) which has been often made use of since by lecturers upon the subject. The diagram is very similar to the one used five years

previously, by Spring (p. 178) for his classes but not brought to the notice of the general chemical public.

Reynolds seized upon what he regarded as the most salient features of the periodic law for representation.

- 1. The transition *per saltum* from one seven to another *e. g.*, chlorine to potassium etc.,
- 2. The fourth element in each series, in general, possesses properties which a transition member might be expected to possess. Thus silicon might be represented as the apex of a tolerably symmetrical curve which should represent for the particular period the direction in which the properties of the series of elements vary with rising atomic weight. A physical analogy will help to make the meaning of this clear. See Fig. 1.

Let the line A B represent part of a string in tension, and a, b, c, d, e, f, g, seven knots upon it. The string is now thrown into a number of vibrating segments: o and o' represent two nodal points between which one segmental vibration takes place. The several knots oscillate rapidly to and fro in the direction of the dotted lines, amoving from the position of rest to a and back again, when it swings to the same extent on the opposite side of the line AB, returns and starts afresh. Each knot performs similar journeys, but the lengths of the paths vary: then the length increases from a to b, from b to cand from c to d, while it diminishes from d to e, e to f, and f to g. The knot d is therefore exceptional, in that it suffers the maximum displacement from the mean position: the knots c and e perform journeys of comparable length but they are otherwise in more or less direct con-



trast: similarly b and f, a and g, form contrasted pairs.

Let the knots in the string represent the atomic groupings we call elements arranged in the order of atomic weight (not necessarily symmetrical, as in the case of the knotted string) rising from a to g and we have a picture of a period of seven elements regarded as a vibrating system. The elements corresponding to d at its maximum displacement he called meso-elements. He noted, in examining the periods:

- 1. That the three elements of lower atomic weight than the *meso-elements* are electro-positive in character while those of higher atomic weight are electro-negative.
- 2. That the numbers above and below the *meso-ele-ments* fall into pairs of elements which, while exhibiting certain analogies, are generally in more or less direct chemical contrast.

He noted, further, that valence alone is an untrustworthy guide to the probable position of an element in a period.

"The pairs of more or less contrasted elements may be likened to the pairs of knots on the string whose paths of vibration are of approximately equal length; but it is convenient for the purpose of graphic illustration to assume that the paths of each pair are of the same length or that the displacements are in the ratios of 1: 2: 3: 4,—that of d, Fig. 1, which is the longest. On reference to the diagram, Fig. 1, the nature of this arrangement will be evident, and the portions when connected as shown are seen to form an expanding curve such as

would be afforded by a string or chain whose parts are in unequal tension.<sup>1</sup>

"With the aid of the scale AB there is no difficulty in picturing the elements in the position of the knots on the string, and so regarding them as members of a vibrating system. All the elements whose constants are well-known find places on the curve. Thus the physical analogy helps us to form some conception of the relations of the members of the periods and of the latter to one another. Moreover the admission of the periodic principle at all seems to require the recognition of similar relations to those indicated.

He mentioned as points brought out by the scheme:

- 1. The transition per saltum disappears as a difficulty.
- 2. Hydrogen is in the Mendelèeff table the first member of a period of seven, the remaining six being unknown. If the form of the curve is allowed to influence the judgment the position of hydrogen in reference to that of lithium is rather that of the last member of one period to the first of another.
- 3. The odd and even periods of Mendeléef are at once distinguished.
- 4. The general contour of the curve is such that we are not permitted to assume the existence of Mendeléeff's ninth period. Six out of the seven elements tabulated by Mendeléeff are unknown.

<sup>1</sup> Prof. Fitzgerald suggested that a vibrating metallic chain, suspended from the ceiling and attached to the floor, would afford a more complete picture, as the regular and considerable changes of tension, due to the increasing weight, would lead to the production of regular expanding loops.

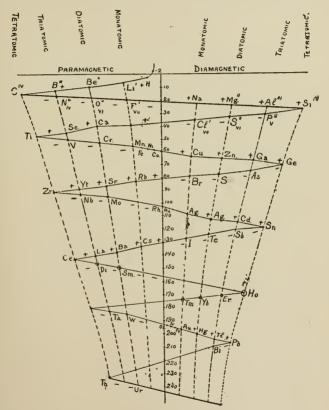
5. The elements which form Mendeléeff's eighth group are found near to three of the ten nodal points. These bodies are obviously interperiodic, in the sense that their atomic weights all exclude them from the periods into which the other elements fall while their chemical relations with certain members of the adjacent periods lead to the conclusion that they are interperiodic in the special sense of being transitional as well.

Notwithstanding the exclusion of Mendeléeff's ninth period the diagram shows that a considerable number of elements are still required to complete the system, in the opinion of the author.

131. Crookes' Modification of this Diagram.—Crookes, (156) in a lecture before the British Association, reproduced this diagram of Reynolds, with certain modifications which may be seen in the accompanying figure. He explained at some length, the coincidences and other features of the diagram.

As to the gaps in Mendeléeff's table, he said: "I do not, however, wish to infer that the gaps in Mendeléeff's table, and in this graphic representation of it, necessarily mean that there are elements actually existing to fill up these gaps; these gaps may only mean that at the birth of the elements there was an easy potentiality of the formation of an element which would fit into the place."

He further said that the symmetry of nearly all this series proclaims at once that we are working in the right direction. The anomalies are explained as springing from imperfect knowledge of the elements and their atomic weights. He added: "The more I study the arrangement of this zig-zag curve, the more I am con-



vinced that he who grasps the key will be permitted to unlock some of the deepest mysteries of creation. Let us imagine if it is possible to get a glimpse of a few of the secrets here hidden. Let us picture the very beginnings of time, before geological ages, before the earth was thrown off from the central nucleus of molten fluid. before even the sun himself had consolidated from the original protyle. Let us still imagine that at the primal stage all was in an ultra-gaseous state, at a temperature inconceivably hotter (the author says he is constrained to use such terms as temperature, radiation, and cooling but does not like the idea of the periodic motions thus required of the protyle) than anything now existing in the visible universe; so high, indeed, that the chemical atoms could not yet have been formed, being still far above their dissociation point. In so far as protyle is capable of radiating or reflecting light, this vast sea of incandescent mist, to an astronomer in a distant star, might have appeared as a nebula, showing in the spectroscope a few isolated lines, fore-casts of hydrogen, carbon and nitrogen spectra.

"But in course of time some process akin to cooling, probably internal, reduces the temperature of the cosmic protyle to a point at which the first step in granulation takes place: matter as we know it comes into existence, and atoms are formed. As soon as an atom is formed out of protyle it is a store of energy, potential (from its tendency to coalesce with other atoms by gravitation or chemically) and kinetic (from its eternal motion.) To obtain this energy the neighboring protyle must be refrigerated by it and thereby the subsequent formation of other atoms will be accelerated. But with the birth of

atomic matter the various forms of energy, which require matter to render them evident, begin to act; and amongst others, that form of energy which has for one of its factors what we call atomic weight. Let us assume that the elementary protyle contains within itself the potentiality of every possible combining proportion or atomic weight. Let it be granted that the whole of our known elements were not at this epoch simultaneously created. The easiest formed element, the one most nearly allied to the protyle in simplicity, is first born. Hydrogen, or shall we say helium, of all the known elements the one of simplest structure and lowest atomic weight, is the first to come into being. For some time hydrogen would be the only form of matter (as we know it) in existence, and between hydrogen and the next formed element there would be a considerable gap in time, during the latter part of which the element next in order of simplicity would be slowly approaching its birth-point: pending this period we may suppose that the evolutionary process which soon was to determine the birth of a new element, would also determine its atomic weight, its affinities, and its chemical position.

"In this way it is conceivable that the succession of events which gave us such groups as Pt, Os, and Ir; Pd, Ru, and Rh; Fe, Ni, and Co, if the operation of genesis had been more greatly prolonged, would have resulted in the birth of only one element in the place of these groups. It is also probable that by a much more rapid rate of cooling, elements would originate even more closely related than are Ni and Co, and thus we should

have formed the nearly allied elements of the cerium, yttrium and similar groups; in fact, the minerals of the class of samarskite and gadolinite may be regarded as the cosmical lumber-room where the elements in a state of arrested development, the unconnected missing links of inorganic Darwinism, are finally aggregated.

"I have said that the original protyle contained within itself the potentiality of all possible atomic weights. It may well be questioned whether there is an absolute uniformity in the mass of every ultimate atom of the same chemical element. Probably our atomic weights merely represent a mean value around which the actual atomic weights of the atoms vary within certain narrow limits.

"Each well-defined element represents a platform of stability connected by ladders of unstable bodies. In the first accreting together of the primitive stuff the smallest atoms would form, then these would join together to form larger groups, the gulf across from one stage to another would be gradually bridged over, and the stable element appropriate to that stage would absorb, as it were, the unstable rungs of the ladder which lead up to it. I conceive therefore that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that while the majority of the calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on. We are here reminded of Newton's "old worn" particles.

"Is it not possible, even feasible, that these heavier or

lighter atoms may have been in some cases subsequently sorted out by a process resembling chemical fractionation? This sorting out may have taken place in part while atomic matter was condensing from the primal state of intense ignition, but it also may have been partly effected in geological ages by successive solution and reprecipitations of the various earths."

The author then reported some of his own work upon the fractionation of the earths present in samarskite and gadolinite and the spectroscopic work done upon them as "apposite to this question." The theory is then pressed a step or two further to elucidate the matter of elemental evolution and the diagram is again called into use.

In the undulating curve of the diagram he recognized two forces, one acting in the direction of the vertical line and the other pulling backwards and forwards like a pendulum. The vertical line may represent temperature, sinking from the dissociation point of the first formed element to that of the last. The oscillating line must be intimately connected with electricity from the peculiar properties, atomicity, electro-positive and electro-negative characters which it confers. He further assumes that it is identical with chemical energy.

"The elements formed would not all have the same stability, some would be unable to endure the slightest disturbance of the unstable equilibrium in which they took their rise; others would endure longer but would ultimately break down as temperature and pressure varied." He incorporated in the diagram the observation of Carnelley that the elements in the even series of Mendeléeff are paramagnetic and those in the odd series are diamagnetic but acknowledged that there are exceptions, as indeed can be seen in his diagram, and that our knowledge on this point is imperfect.

When the temperature on the vertical line sinks below the dissociation point of uranium, the author thought it possible that the elements began to unite and compounds were formed. At a temperature higher than the dissociation point of hydrogen he mentioned the possibility of the existence of elements of negative atomic weight as called for by Carnelley. He quoted from Helmholtz (Faraday Lecture 1881.) "If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity" and he suggested electricity as one of the negative elements and luminiferous ether as another.

This genesis of matter was then extended to the whole cosmic system. Dr. Crookes was careful to point out that there is no direct proof of such a genesis of the elements and called it a "provisional hypothesis."

132. Crookes' Genesis of the Elements.—A few months later (163) Crookes followed up this same subject in a lecture delivered before the Royal Institution upon the "Genesis of the Elements." In this he examined first into the occurrence of the elements. Bodies are found grouped together in definite proportions with other bodies from

which they differ exceedingly and to which they are held by affinity more or less strong. To separate them that affinity must be overcome. The combined bodies usually differ very widely in their atomic weights.

Again bodies are found associated with others closely allied to themselves. They are not held together by any decided affinity nor in definite proportions and their atomic weights are often almost identical. They show similar behavior towards chemical reagents and this renders their separation difficult. The most striking instance of such occurrence is found in the case of the so-called rare earths.

The method of separating these by fractionation was given in outline and then the method of examining, by means of the spectroscope, the light given off by these purified simple bodies under the action of induction sparks in a high vacuum. The complicated and puzzling nature of these spectra was mentioned. The spectrum given by an element was regarded as an unalterable index of that element. If yttrium, one of the rare earths, be fractioned by prolonged and careful work it is separated into the extremes which differ chemically from yttrium and more markedly from one another, yet all give the same spectrum.

As an explanation the following view is offered. Between the molecules we are accustomed to deal with in chemical reactions and the ultimate atoms as first created, come smaller molecules or aggregates of physical atoms: these sub-molecules differ one from another, according to the position they occupied in the edifice. To illustrate,

the yttrium may be represented by a five shilling piece. By chemical fractionation it is divided into five separate shillings. These are seen to be not counterparts but, like the carbon atoms in the benzene ring, have the impress of their position 1, 2, 3, 4, 5, stamped upon them. If these shillings are examined by a more powerful agent, e. g., thrown into the melting pot, they all turn out to be silver. So the yttrium and its fractions all under the electric spark give the same spectra though they give different phosphorescent spectra. Another hypothesis is that here are new chemical elements differing so slightly in properties as to admit of only imperfect separation. Then it is shown that the original spectrum can be reproduced by using appropriate mixtures and hence that it may be caused by a constant mixture and is not necessarily indicative of a single element. Crookes made mention of the fact that Lecoq de Boisbaudran refers the phosphorescent spectra to impurities in the preparation.

He also referred to the remarkable discovery of Nordenskiold¹ who had been working along the same line as himself. This was that the oxide of gadolinium, though it is not the oxide of a simple body, but a mixture of three isomorphous oxides, even when it is derived from totally different minerals found in localities far apart from one another, possesses a constant atomic weight. This is a new fact in chemistry that three isomorphous substances derived from different elements occur in nature not only always together but always in the same proportious.

<sup>&</sup>lt;sup>1</sup>Comp. Rend., Nov. 2, 1886.

"What is true of yttrium and of gadolinium may be assumed as true of all elements. In some (possibly in all) the whole spectrum does not emanate from all their atoms but different spectral rays may come from different atoms and in the spectrum, as we see it, all these partial spectra are present together. This may be interpreted to mean that there are definite differences in the internal motions of the several groups of which the atoms of a chemical element consist. Another important inference is that yttrium atoms, though differing, do not differ continuously but *per saltum*."

The discovery of the composite nature of didymium by Welsbach was alluded to. "If we only had the right methods, why could not calcium and others be decomposed." He "ventures provisionally to conclude that the so-called elements, or simple bodies, are in reality, compound molecules." The author then by means of the primal element protyle and the force electricity constructed the various elements, using the Reynolds diagram as described in the preceding section, the latter portion of this lecture being a repetition of the one before the British Association.

## 133. Dulk upon Gravitation and the Atomic Weights.

—Gravitation is so far as known a property of the atoms, said the author, (157, 158) and furthermore the only property which in its influence upon the atom, as shown in the atomic weight, furnishes the one unchangeable characteristic of the atom. "This being the one unchanging property of the atoms there have been many attempts at solving the relations existing between them. It is

necessary now to form an hypothesis which will give the relations of the atoms to gravitation." The effort to do this is based upon the alkali metals. It is presupposed that the atoms do not consist of different quantities of matter of the same kind but that each atom, differing chemically, consists of a peculiar matter, a condensation of the cosmic ether. If the atoms are represented as circles then certain ratios can be detected between the squares of the radii of two or more of the circles which correspond with the differences of successive members of the same family or corresponding members of different families. The ratios of the atomic weights can be represented by geometrical figures, for which reference must be made to the original articles.

134. Phipson's Outlines of a New Atomic Theory.—In a singular phamphlet, the author stated (159): "The old notion that matter is composed of atoms and spaces is doubtless correct and it can be argued successfully that atoms are extremely minute spheres. The space between the atoms is filled with phlogiston."

The law of volumes is reversed by the author after this fashion: "Equal gaseous volumes contain a different number of atoms all of the same size and same weight. This implies that the atoms are all of the same nature and proclaims the unity of matter. Whatever substance may be under consideration its atoms are all of the same nature, and they are separated by space, which we call phlogiston, a term that implies movement, light, heat, electricity, etc. The greater the amount of

phlogiston the greater the energy of the system of atoms termed an element."

The matter of all the elements is therefore identical; the phlogiston alone varies, that is, the space between the atoms (considered at rest) or their extent of motion. A chemical element is therefore a system of atoms, the properties of which depend upon its phlogiston and the amount of the latter is deduced from the weights which combine together."

The author then offered explanations of various phenomena, allotropism, galvanic couples, etc. No experimental nor other proof is offered for his theory.

- 135. Reed's Graphical Representation of the Relation between Valence and Atomic Weight. Reed (164) started with three hypotheses which were first announced though in a different manner, by Johnson.
- 1. The valence of an atom is its capacity for electropolarity.
  - 2. The polarity of an integrant molecule is always zero.
- 3. Positive and negative changes of polarity are always cotemporaneous and equal.

All the atoms in a molecule are to be considered as polarized, one half the atoms (measured in valence not in numbers) positively and the other half negatively; an atom is neutralized when it is united with one or more atoms having the same degree of polarity but of opposite sign, neutralization meaning opposition and not that the polarity is destroyed. The atomic weights and observed valence of the elements are given and the principal compounds in which those valences occur. In compounds

which can not be electrolyzed, the more basic elements are considered electro-positive and the more acid electronegative.

The diagram is plotted as follows: Two straight lines meet at right angles at zero, the vertical line representing valence multiplied by ten and extending to 40 below zero, and the horizontal line representing the atomic weights; a point is located on the planefor the maximum, minimum and characteristic valence of each element, and nearly all these points are found to lie on a double series of parallel lines, the successive pairs of which are separated by equal distances. The deviations from these positions is so slight as to be barely noticeable on the scale used.

It was found that the loci of two equations, y = a (x-4) and y = a(x-5), pass through or near the

points corresponding to more than fifty of the elements whose physical characteristics are most accurately known; provided the plane is wrapped around a cylinder having its axis parallel with the axis of abscissae and its radius  $R = \frac{8a}{\pi}$ . The loci of these equations now become parallel helices, that cut the axis of abscissae at intervals of sixteen units of atomic weight. The ordinates become arcs of circles formed by planes cutting the cylinder at right angles to its axis. The axis of abscissae becomes an element of the surface of the cylinder. The circumference of the cylinder measures eight units of valence. Valence is measured upward from the axis of abscissae, if it is positive, and

downwards, if it is negative. The full development of this system requires an entire group of hitherto undiscovered elements to which peculiar properties are ascribed. The number is fifteen and the valence would be either eight or zero; they would be volatile and non-atomic, etc. The arrangement resembles that of Gibbes, in some respects, more closely than that of de Chancourtois. The idea of the helix is, of course, an old one. In this instance it is more thoroughly worked out than in previous attempts.

After considering the diagram and pointing out some periodic and recurrent combinations, Reed concluded that, "saturation valence is an equi-crescentrotatory function of the atomic weight" and in order to represent this idea graphically he located the points on the surface of a cylinder instead of on a plane. He next pointed out that he had considerable grounds on which to base the conclusion just quoted, which he claimed could hardly be a coincidence from the fact that it united not less than fifty of the chemical elements by so simple a relation between valence and atomic weight. Whether this conclusion was or was not the expression of a natural law he left for others to decide after mature consideration.

136. Gruenwald's Mathematical Spectrum Analysis. —During the years 1887 and 1888, Grünwald published three papers (165) in the Astronomische Nachrichten and the Monatshefte für Chemie upon the mathematical relations or coincidences of the spectra of water vapor, oxygen, hydrogen, magnesium, cadmium and carbon. The object of these investigations was to discover

relations between the elements by means of the spectra, and, if possible, in this way to reduce them to their simpler components or fundamental elements. His method of work was to compare the groups of lines in any two chemical elements under consideration. He concluded that they have a common component if a group of lines in one when multiplied by a simpler number gave the lines of a group in the spectrum of the other element. This numerical factor was thought to give the ratio of the volumes occupied by the common constituent in unit volumes of the two substances.

In this way formulas can be calculated for the different elements. Thus in the spectrum of hydrogen there are two groups of lines a and b which multiplied by  $\frac{19}{30}$  and  $\frac{4}{5}$  give corresponding groups in the spectrum of water, and, since hydrogen has  $\frac{2}{3}$  of the volume of water the equations are gotten; a+b=1;  $\frac{19}{30}a+\frac{4}{5}b=\frac{2}{3}$ ;  $a=\frac{4}{5}$ ;  $b=\frac{1}{5}$  and the formula for hydrogen is  $ba_4$ . Grünwald called the substance a, coronium, and b, helium. For oxygen he gave the formula  $H'b_4$  ( $b_4c$ ) where c is a new substance, though he afterwards considered c merely a in a different state of compression.

Adopting the water spectrum as a standard he gave various means of recognizing the presence of these primary elements a and b in the various spectra. These criteria he applied to the spectra of carbon, magnesium, and cadmium and found them made up of the two elements a and b in different states of compression. Grünwald used various factors for the transformation of these groups of lines. The groups of lines of the shortest

wave-lengths are connected with the substance b and the greater wave lengths with a. An examination of a number of the elements convinced him that "many, perhaps all, bodies hitherto considered as elements were compounds, composed of condensation forms of the primary elements a and b, of hydrogen  $= ba_*$ , in various physical modifications." This theory he supported by a great array of confirmatory measurements and, as has been said, he connected these two substances with the remarkable color spectrum line helium and the well-marked line of the sun's corona, coronium, regarding both as constituents of hydrogen gas.

137. Ames' Criticism of Gruenwald.—This work of Grünwald attracted a good deal of attention. The conclusions were regarded as highly probable by Liveing and Dewar but met with strong criticism from an American source. This was Joseph S. Ames of the Johns Hopkins Physical Laboratory (185). His criticism was as follows: "There are two distinct questions to be answered: (1) Are there any numerical relations connecting the spectra of the elements? and if so, (2) What is the meaning of the fact? Cornu, Deslandres and others have long since answered the first question for us, but whether Dr. Grünwald's answer to the second one is correct or not depends upon the completeness with which the numerical relations hold for the entire spectra of the substance. It is here that Dr. Grünwald's work can be criticized.

"As noted, the spectrum of the oxy-hydrogen flame is used to test the existence of lines belonging to a and b. By far the most accurate and complete determination of

this spectrum is that of Liveing and Dewar' but this does not always answer Dr. Grünwald's purposes. the British Association Report for 1886 there is a provisional list of lines of the water spectrum which he often uses, although the wave-lengths have since been corrected. Further if other lines are necessary, they are found by halving the wave-lengths of the secondary spectrum of hydrogen. Many lines thus determined are actually present in the water-spectrum but why are they not all there? Dr. Grünwald says it is because the amplitude of vibration of parts of the molecule can be so changed, owing to the presence of other substances, that the intensity may increase or diminish or become too faint to be observed. To this argument there is absolutely no answer. In some cases, too, the average of two wave-lengths is used as a criterion of a wave length of b which falls between them. And as a last resort, if the necessary wave length can not be found in the water spectrum by any of these means, it is put down as "new" and is called an "unobserved" line. As just shown, Dr. Grünwald easily explains why the strongest lines in the spectrum of an element, cadmium for example, when "transformed" into water lines, may be faint; and vice versa. But how does he account for the fact that double lines are not transformed into double lines? This seems to me a fundamental objection. The concavegrating gives the only accurate method of determining the ultra-violet wave lengths of the elements; and as a consequence of not using it, most of the tables of wave-

<sup>1</sup> Phil, Trans., 1888,

lengths so far published are not of much value. So Grünwald's error may be great. And, besides when we consider that in the water-spectrum as given by Liveing and Dewar, without the help of the secondary spectrum of hydrogen, there is on the average one line for every two Aengström units, it would be remarkable indeed if any law could not be verified. This is strikingly shown in the first group of the cadmium lines. Here 6742 and 6740 are two readings for the wave lengths of the same line, as made by two observers: yet Grünwald finds a water-line for each of them.

"The fact that there are exact numerical relations connecting the spectra of different elements does not afford a proof of Grünwald's hypothesis; and, until the above difficulties are removed, the evidence is against it. But even granting it, how do we know that a and b are not themselves compounds? In the second group of cadmium lines there are nineteen lines which can be transformed into b lines; b has many other lines; so at the most this only shows that cadmium and b have a common constituent, unless, of course, the absence of the other cadmium lines is accounted for in Grünwald's own way of varying intensity.

"The lines of the spectrum of any one substance, as carbon or iron, seem to fall into definite series or groups; and the wave-lengths of the lines in these groups can be expressed by formulas, as is well known. All that the fact of there being a connection between the spectra of different substances seems to show is then, that there may be a formula common to many elements, as Kayser

and Runge have recently found. And all that this means is that the molecules of these elements vibrate in general according to a similar law."

is perhaps in place to give here Grünwald's definition of chemical atoms (176): A chemical atom is a complex of exceedingly many moveable particles, which are elastic, but so intimately connected together that no chemical process which comes under our consideration is capable of severing this union and breaking the atom into fragments. The parts of the atom are not conceived of as absolutely immutable any more than the atom itself, but as capable within finite limits of undergoing modifications, which have definite relations to their mutual reactions.

"According to this view an atom may have a spectrum consisting of very numerous rays of different wave-lengths. This spectrum varies according to fixed laws, when the chemical condition of the substance consisting of such atoms and its relations to other substances vary. It is not impossible, and even probable, that the particles of an atom are identical with the particles of the ether, or with condensation forms of the ether. It will be easily seen that in an intimate union of two atoms, in which they combine each with one or with several adjacent particles, the latter, which possibly in the free condition of the atoms perform vibrations of different periods, after the chemical combination of the atoms, vibrate in an accordant manner, and may thus become true moveable nodal points or ramification points of the molecules of

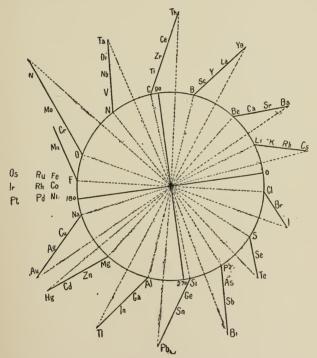
the compound in question. This will find its expression in the spectrum of the compound in such a manner that it will have rays belonging to each component; on the disruption of the compound they will generally be resolved into two rays of different periods, one of which belongs to the spectrum of one of the constituents now set free, and the other ray to the spectrum of the other constituent."

130. Thomsen's Views as to the Unity of Matter.—It is a striking fact that two such distinguished chemists as Thomsen and Wislicenus should, in the latter part of this century deem it especially fitting in commemoration of historical anniversaries of their respective universities to give expression to their views as to the unity of matter. Thomsen (168) first reviews the history of this Then he takes up the question for great idea. himself as to whether all of the seventy elements. now recognized, are to be looked upon as one kind of matter. The plausibility of this hypothesis is discussed from the standpoint of the distribution of the elements; the comparison of them with the compound radicals; the vast number of organic compounds which are made up of four of these elements only; the close approximation of the atomic weights to integral numbers; the dependence of the properties upon the atomic weights; the fact that some of these elements have been separated into others, as didymium; and the hope of further success along the line of fractional precipitation. He noted that the atomic weights were not consecutive whole numbers but often differ by a few units. Like de Chancourtois and Meyer he imagined these elements upon a symmetrical cylinder, the elements of the same valence falling in vertical columns. The temperature of the sun, he thought, ought to decompose the elements, at least as far as the atoms and perhaps to the elementary matter. The helium line, seen in the sun's spectrum, must be lighter than hydrogen and may be the stuff out of which all the others are formed. Something like this temperature might be obtained by concentrating the sun's rays. The isolation of the elementary matter would be a very difficult problem, however, the isolation of the ordinary elements being often very difficult. Lastly, he compared the change of matter from one kind to another with the problem of the biologist with regard to the change of series.

140. A Function expressing the Periodicity of the Elements by Flavitzky.—The graphical representations of the periodic law by Bayley, vonHuth, Spring and Reynolds are all mentioned by Flavitzky as (166) curves which cannot be represented by simple mathematical equations. The discovery of the equation would enable one to accurately determine the atomic weight and therefore he attempted to give an approximate solution of the problem. For this purpose he divided the elements up into periods, the first containing the 7+7 elements from lithium to chlorine. The properties of these are discussed and compared. The second period consists of 7+3+7.

Sine and cosine functions will not do for the Periodic Law, among other reasons, because the values do not change sign + or —in passing through o°. Flavitzky

says the periodic law must be represented by some function of tangent or cotangent. If these functions are used, then the periodic law can be graphically repre-



FLAVITZKY'S DIAGRAM.

sented by a circle or curve with a circumference in which seven elements would be found in the first semi-circumference and seven in the second. The diagram will make this clear. The function decided upon is then given as

a cot g  $2\pi \varphi(p)$  where a is a constant depending on the properties which so far have not been expressed numerically and  $\varphi(p)$  is dependent on the atomic weight. Neglecting the  $\infty$  value of the contagent when the angle is  $0^\circ$  he assumed the first semi-circumference as having a value of 37-1.4=35.6.

Taking the equation  $a \cot g \ 2\pi \frac{p-1.4}{35.6}$  and solving it so

that  $a \cot \frac{\pi}{2} = 0$ , he found that p = 10.3 and this value

lies between beryllium and borou. Therefore, in the first quadrant there are two elements lithium and beryllium, leaving in the second quadrant the remaining five. Similarly when  $a \cot \pi = \infty$ ; p = 19.2 that is just beyond the atomic weight of fluorine. Continuing around the

circumference,  $a \cot \frac{3\pi}{2} = 0$ , when p = 28.1; that is, between silicon and phosphorus and finally  $a \cot 2\pi = \infty$  when p=37. The next period is worked out in like manner.

The function fails with the eighth group and after cæsium all is more or less guess-work. The figure is not drawn to scale but is merely intended to show something of the nature of the graphic representation. Instead of giving only two elements in the first quadrant, as stated above, three are given. In discussing the diagram he connected the changes in the electropositive or negative character of the elements in the various groups with the changes in the sign of the cotangent from 0° to 90° +; from 90° to 180°—; etc., and we have a repetition of these signs as the darius vector sweeps out a larger and larger circular

angle. The lack of strict repetition of properties in the higher periods he assumed to be due to the greater complexity of the molecules of the elements with higher atomic weights, the non-correspondence strictly of sodium with copper, silver, and gold being cited. He added some speculations as to the cause of valence and chemical affinity, assuming that the molecules were not all moving in the same or parallel planes and further in these planes the molecules move either clockwise or counterclockwise and that when two elements combine the motions of the molecules take place in planes more or less inclined to each other. He elaborated this idea and pictured the relative planes in which the atoms are assumed to move. Thus sodium and fluorine are in parallel planes but the motions are opposed. He supposed that when the planes in which two elements move are not parallel, the contrary motions are resolved, so that the component motion parallel to the other plane causes the affinity. This speculation is purely tentative.

141. Numerical Regularities observed by Bazaroff.— The author (167) found that the variation in the numbers expressing the atomic weights of the elements, arranged according to the periodic system, is analogous to the changes in the properties of the elements and their compounds.

In the periodic system of the elements, either in the vertical or horizontal lines, if the atomic weight of an element be divided by that of the element having the next lower atomic weight, products are obtained which decrease regularly with the increase in the atomic weights

compared. In the horizontal series the maximum is found to correspond with the ratio  $\frac{Be}{Li} = \frac{9.08}{7.01} = 1.2953$ , the minimum with  $\frac{Bi}{Pb} = \frac{207.5}{206.30} = 1.0054$ . This decrease is not continuous, there being alternate decrease and increase: Thus  $\frac{Mg}{Na} = 1.0411$ ;  $\frac{Al}{Mg} = 1.1295$ ;  $\frac{Si}{Al} = 1.0355$ ;  $\frac{P}{Si} = 1.1057$  etc. Represented graphically this gives a zigzag curve (atomic weights as abscissae, quotients as ordinates.) The author expressed this as a law thus: "the increase in the atomic weights of the elements proceed, with a variable intensity, the smaller coefficient of change varying with the larger in such a way that both regularly decrease."

Another regularity is observed in the vertical groups, for example, with the coefficients in the second groups.

The author expressed this change by another law "In the vertical series in the periodic system, the relations of two neighboring atomic weights, decreases with increasing atomic weight, but this decrease is alternately larger and smaller."

Neither of these laws extend to the entire system as many of the atomic weights are too imperfectly known as yet. Still the author regarded it as possible to state the following general law: "The magnitude of the atomic weight of each element is determined by the magnitude of the atomic weights of the elements next to it in the periodic system both horizontally and vertically." Not-

withstanding the apparently complicated character of the relation pointed out, the author thinks that "when the fundamental data are more exactly determined, it may be possible to calculate the atomic weight of an element with greater accuracy than is the case at present."

offered by Livermore (171) is based upon the divisibility of the atomic weight by two, in conjunction with the increase in these weights. The object is to contribute to the removal of the difficulties urged by Wurtz against the Periodic Law, namely that the atomic weights of successive elements vary within considerable limits without displaying any regularity in these variations and that the graduations in properties do not seem to depend upon the degree of the differences between the atomic weights.

The series were first examined for evidences of a constant increase. Using 4 as a modulus, he secured two series:

This embraces in two parallel series all the terms of the first three periods of Newlands and Mendeléeff with the exception of 9, and 14, that is twenty-two out of the twenty-four. These two series coincide with the perissads and artiads already distinguished by chemists because of their uneven and even quantivalence. He therefore called it the Perissad Law. By similar methods the numbers between 70 and 100 fall into two series with a common difference of 5 for the perissads and per-

haps 4 for the artiads (the latter series indefinite.) Between 100 and 150 the perissads increase regularly, with a common difference of about  $6\frac{1}{4}$  and the artiads less regularly with the same difference.

Beyond this the author thought the atomic weights were too imperfectly known for accurate classification. The fact that these arrangements apparently throw cobalt, nickel, and mercury out of their proper groupings was mentioned. Tables are given containing the serial numbers, the observed atomic weights and the deviations from the serial numbers. Other columns show the specific gravity, the atomic volume, the fusibility, malleability and other properties. The possibility of the existence of elements with the atomic weights 15, 43, or 44, 47, 60, and perhaps of 99, 100 and 143 is inferred from analogy.

The formula for calculating the atomic weights is a + nd and it has the following values for the several groups of common differences,  $6.99 + n \times 4.02$ ;  $12.00 + n \times 4.01$ ;  $70.25 + n \times 4.85$ ;  $74.88 + n \times 4.12$   $107.85 + n \times 6.20$ ;  $105.98 + n \times 6.22$ .

A good deal of importance seems to be attached to the electro-chemical factors assigned to each element. The bearing of these is not very clear.

- 143. An Atomic Hypothesis by Pearson.—This paper (172) is largely mathematical, dealing in the nature and motion of the atoms. Simple numerical relations, periodicity, etc., are not taken into consideration.
- 144. Johnstone Stoney's Logarithmic Law of the Atomic Weights.—This memoir (173) is divided into five sections:

Section 1. Shows that it is impossible to discuss the mathematical relations between the successive atomic weights by plotting down the atomic weights as ordinates and allowing the abscissae to represent some simple numerical series. The curve would be represented by the equation  $y = k (\log x)^{\frac{1}{2}}$  where x does not represent simple integral numbers but a circular function of them. The method is therefore a hopeless one.

Section 2. Here successive atomic weights are represented not by lines but by volumes. A succession of spheres are taken whose volumes are proportional to the atomic weights (atomic spheres.) When the radii of these spheres are plotted as ordinates and a series of integers as abscissae, the general form of the logarithmic curve  $y = k \log (qx)$  becames apparent. Close scrutiny has shown that this expresses the law of nature. It is the central curve that threads its way through the positions given by observations and the deviations from it of the positions assumed by the actual atomic weights will be included by making x a circular function of integral numbers, instead of those numbers themselves. issue of the investigation is to show that when such a diagram is formed with ordinates which are the cube roots of the atomic weights, referred to hydrogen as unit, so that the ordinates may be the radii of spheres whose volumes represent the atomic weights, then:

1. The logarithmic curve  $y = k \log (ma)$ ,  $\log k = 0.785$ ,  $\log a = 1.986$ , threads its way through the positions plotted down from the observations.

- 2. In the case of the perissads, the complete curve which includes their perturbations from the central curve is  $y_{\rm m}=k\log (a\ m+\frac{1}{3}\ \sin\frac{m\pi}{27}+\frac{1}{3}\ \sin\frac{m\pi}{18} + {\rm subsequent\ terms})$ , the next term being probably either  $-\frac{1}{2}\sin\frac{m\pi}{9}$  or  $-\frac{2}{3}\sin\frac{m\pi}{9}$ .
- 3. The form of the function representing the perturbations of the artiads is different, at all events, after the third term.

Section 3. There are other neighboring curves (log-arithmic) which pursue a course close to the observed position and the method adopted in dealing with these curves is described and the grounds on which they have been successively excluded are stated. The evidence relied on has been for the most part, that the perturbations from them are less reducible to order.

Section 4. The curve finally selected is thrown into a polar form and furnishes a diagram for laboratory use. "It presents conspicuously the information which the Mendeléeff table is capable of supplying with the further advantage of placing before the eye an intelligible representation of the atomic weights."

145. New Relations between the Atomic Weights observed by Delauney.—In his first paper (174) Delauney states that if the equivalent of hydrogen be taken as unit the equivalents of the other elements are represented by the expression  $\frac{N}{3}\sqrt{s^2-n^2}$  in which N and n are whole numbers, the value of n being 0, 1, 2, 3, or 4.

The calculated numbers agree fairly well with actual determinations. The elements may be divided into groups or families according to the values of n, but the same element may fall into two or even three families.

The omission of  $\frac{N}{3}$  merely changes the unit of equiva-

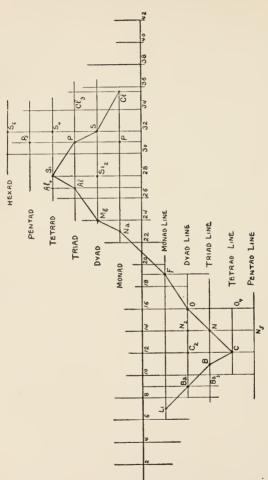
lence, and hence only the simplified expression  $\sqrt{s^2-n^2}$  need be considered.

The author supposed the existence of a primitive molecule composed of five atoms revolving at different distances around a central atom after the manner of planets around the sun. If such a system is penetrated by a group of atoms, all tangent to one another, the opposite directions of their motions will give rise to a stress which will result in an agglomeration of the atoms.

In another paper, Delauney (186) observed that when the elements are arranged in the order of their atomic weights each atomic weight differs from that immediately preceding it by the square root of a whole number. This number is variable, but is always harmonic, that is, contains as primary factors only the numbers 1, 2, 3, and 5.

146. Haughton's Geometrical Illustrations of the Periodic Law.—This work (175) is based upon the diagram of Reynolds. Taking the first fourteen elements and eliminating C, N, O, Mg, and Si as being upon a straight line, a serpentine cubic curve may be drawn through the remainder. (See figures 1 and 2.) Similarly for the second fourteen, five are found upon a

FIGURE I. (HAUGHTON).



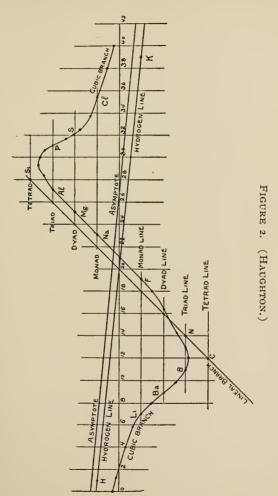
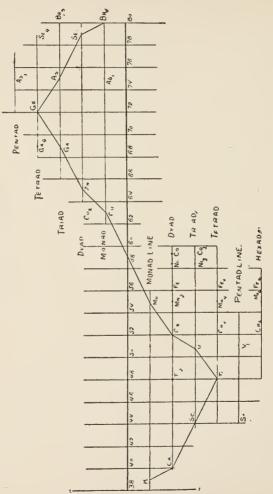


FIGURE 3. (HAUGHTON).



78 20/ 89 TETRAD TRIAD DYAD LINE FIGURE 4. (HAUGHTON). MONAD LINE Drau MONAD TETAADLINE TR. AD LINE 25 CUBIC BRANCH 53 ASYMPTOTE 38

straight line, namely Ti, V, Ca, Ga, and Ce. A much more complex cubic curve can be drawn through the remainder. (See figures 3 and 4).

The relationships of these elements as exemplified by the curves, are pointed out. The position of hydrogen is discussed and Fe, Ni, Co, are taken from the places assigned by Mendeléeff and placed next to chromium. The possibility of the existence of other elements is suggested as, for instance, one of the atomic weight 50 and one of 69.5.

147. Hartley's Definition of Atomic Weight.—An atomic weight is a numerical proportion. There are seventy elements and seventy atomic weights and the serepresent matter in seventy different states of condensation.

The author (177) would recommend the following definition: The atomic weight of an element is the ratio of the mass of its atoms to the mass of an atom of hydrogen. The term atomic weight should be abolished and atomic mass substituted. Similarly, molecular weight should be defined as the mass of a molecule or molecular mass. The mass of a molecule is the sum of the masses of its constituent parts.

The Periodic Law can then be thus stated: The properties of the atoms are a periodic function of their masses. In any graphic representation of the periodic law the fact that it is upon the mass of the atoms that their properties depend should appear prominently. The diagram of Dr. Johnstone Stoney used to illustrate the "Logarithmic Law of Chemistry" has on this account alone a preeminent importance.

148. Stransky's Numerical Relations.—Such numerical relations as the following are given by Stransky (180):  $5+2\times2=7$  (Li);  $5+5\times2=9$  (Be);  $5+3\times2=11$  (B); etc.  $10+1\times2=12$  (C);  $10+2\times2=14$  (N);  $10+3\times2=16$  (O).

The following relation is then stated: "The atomic weights of the elements of any natural group are rational multiples of that of the first member of the series minus a constant or some number regularly increasing in arithmetical progression." From the table given below it can be deduced that the atomic weights of elements of any natural group are rational multiples also of the second member of the series, minus a constant or some number regularly increasing in arithmetical progression.

| Li  | 7  | $1 \times 7 = 7$        |           |
|-----|----|-------------------------|-----------|
| Na  | 23 | $4 \times 7 - 5 = 23$   | 1×23 =23  |
| K   | 39 | 7×7—10 <del>=</del> 39  | 2×23—7=39 |
| Cu  | 63 | 11×7—15 <del>=</del> 62 | 3×23—7=62 |
| Rb  | 85 | 15×7—20=85              | 4×23—7=85 |
| &c. |    | &c.                     | &c.       |

149. Remsen on the Nature of the Elements.—In a lecture upon the "Chemistry of To-day" (183) this author says: "It has been shown by a Russian chemist, Mendeléeff, and at the same time by a German, Lothar Meyer, that the elements are related in a very remarkable way, so closely that it is possible to arrange them all in one table, in which they form parts of a system general. The law governing the variations in properties of the elements is known as the Periodic Law. The limits of this article will not permit any detailed explanation of

this remarkable law. The main point that I wish to emphasize is, that the so-called elements are shown to be related to one another, and it seems impossible in the light of these facts, to believe that they are distinct forms of matter. It seems much more probable that they are in turn composed of subtler elements and it has been pointed out that all the substances which we now call elements, of which there are about seventy, can be conceived to be made of two fundamental elements combined in different proportions. There does not, however, appear to be any immediate prospect of discovering these fundamental substances."

150. Mendeleeff's Faraday Lecture.—This lecture, delivered before the London Chemical Society in 1889, "passing in review the twenty years' life of the generalization which is known under the name of the Periodic Law," is an exceedingly valuable contribution to the history of this system. It gives a brief summary of the work which preceded his, and then of his own beginnings; it gives his criticisms of the work of those who have followed him and something of his views as to the future development of the law.

A portion of the lecture is devoted to proving that it is not possible by the ordinary curves and mathematical formulas to properly represent the periodicity which is, according to the law, to be observed between the properties of the atoms. In the first place, as Hartley has emphasized, this periodicity exists between the masses of the atoms. "All that was known of functions dependent on masses derived its origin from Galileo and Newton,

and indicated that such functions either decrease or increase with the increase of mass, like the attraction of celestial bodies. The numerical expression of the phenomena was always found to be proportional to the mass, and in no case was an increase of mass followed by any recurrence of property such as is disclosed by the Periodic Law of the elements. This constituted such a novelty in the study of the phenomena of nature that although it did not lift the vail which conceals the true conception of mass, it nevertheless indicated that the explanation of the conception must be searched for in the masses of the atoms.

"Now natural science has long been accustomed to deal with periodicities observed in nature, to seize them with the vice of mathematical analysis, to submit them to the rasp of experiment. And these instruments of scientific thought would surely long since have mastered the problem connected with the chemical elements, were it not for a new feature which was brought to light by the Periodic Law and which gave a peculiar and original character to the periodic function. If we mark on an axis of abscissae a series of lengths proportional to angles and trace ordinates which are proportional to sines or other trigonometrical functions, we get periodic curves of a harmonic character. So it might seem, at first sight, that with the increase of atomic weights the function of the properties of the elements should also vary in the same harmonious way. But in this way there is no such continuous change as in the curves just referred to, because the periods do not contain the infinite number of points constituting the curve, but a finite number only of such points. An example will better illustrate this view. The atomic weights of certain elements steadily increase, and their increase is accompanied by a modification of many properties which constitutes the essence of the Periodic Law. But to connect by a curve the summits of the ordinates expressing any of these properties would involve the rejection of Dalton's law of multiple proportions. Not only are there no intermediate elements but, according to the very essence of the Periodic Law there can be none: in fact a uniform curve would be inapplicable in such a case, as it would lead us to expect elements possessed of special properties at any point of the curve. The periods of the elements have thus a very different character from those which are so simply represented by geometers. They correspond to points, to numbers, to sudden changes of the masses and not to a continuous evolution. In these sudden changes, destitute of intermediate steps or positions, in the absence of intermediate elements, we must recognize a problem to which no direct application of the infinitely small can be made. Therefore, neither the trigonometrical functions proposed by Rydberg and Flavitzky, nor the pendulum-oscillations suggested by Crookes, and the cubical curves of Haughton, which have been proposed for expressing the periodic law, from the nature of the case, can represent the periods of the chemical elements. If geometrical analysis is to be applied to this subject it will require to be modified in a special manner."

He spoke of the efforts of Mills and Tchitcherine to ex-

press the atomic weights of the elements by means of algebraic formulas but regarded them as incomplete and said that attempts like these must be multiplied. As to Lockyer's hypothesis he said that it "evidently must have arisen from a misunderstanding. The spectrum of a compound body certainly does not appear as a sum of the spectra of its components; and therefore the observations of Lockyer can be considered precisely as a proof that iron undergoes no other changes at the temperature of the sun but those which it experiences in the voltaic arc, provided the spectrum of iron is preserved. As to the shifting of some of the lines of the spectrum of iron while the other lines maintain their positions, it can be explained, as shown by M. Kleiber<sup>1</sup> by the relative motion of the various strata of the sun's atmosphere, and by Zöllner's laws of the relative brilliancies of different lines of the spectrum. Moreover, it ought not to be forgotten that if iron really proved to consist of two or more unknown elements, we simply should have an increase of the number of our elements. not a reduction and still less a reduction of all of them to one single primary matter."

As to the criticism of the periodic law by Berthelot, he said "he has simply mixed up the fundamental idea of the law of periodicity with the ideas of Prout, the alchemists, and Democritus about primary matter. But the Periodic Law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature

<sup>&</sup>lt;sup>1</sup> Journal of the Russian Chemical and Physical Society for 1885, p. 147.

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of the elements; it does not in the least originate in the idea of an unique matter and it has no historical connection with that relic of the torments of classical thought. and therefore it affords no greater indication of the unity of matter or of the compound nature of our elements, than the law of Avogadro, or the law of specific heats, or even the conclusions of spectrum analysis. None of the advocates of an unique matter have ever tried to explain the law from the standpoint of ideas taken from a remote antiquity when it was found convenient to admit the existence of many gods, and of an unique matter." Referring to the comparison of Pelopidas and others of the periodic system of the elements with the homologous series of the hydrocarbon radicals, he wrote: "The most important consequence which, in my opinion, can be drawn from the above comparison is, that the Periodic Law, so apparent in the elements, has a wilder application than might appear at first sight; it opens up a new vista of chemical evolutions. But, while admitting the fullest parallelism between the periodicity of the elements and that of the compound radicals, we must not forget that in the periods of the hydrocarbon radicals we have a decrease of mass as we pass from the representative of the first group to the next, while in the periods of the elements the mass increases during the pro-It thus becomes evident that we cannot speak of an identity of periodicity in both cases, unless we put aside the ideas of mass and attraction which are the real cornerstones of the whole of natural science and even enter into those very conceptions of simple

bodies which came to light a full hundred years later than the immortal principles of Newton. From the foregoing, as well as from the failures of so many attempts at finding in experiment and speculation a proof of the compound character of the elements and of the existence of primordial matter, it is evident, in my opinion, that this theory must be classed among mere utopias. But utopias can only be combatted by freedom of opinion. by experiment, and by new utopias. In the republic of scientific theories, freedom of opinions is guaranteed. It is precisely that freedom which permits me to criticise openly the widely diffused idea as to the unity of matter in the elements. Experiments and attempts at confirming that idea have been so numerous that it really would be instructive to have them all collected together, if only to serve as a warning against the repetition of old failures."

Mendeléeff spoke of his predictions and their happy fulfilment. He added that "although greatly enlarging our vision, even now the Periodic Law needsfurther improvements in order that it may become a trustworthy instrument in further discoveries." He does not seem to regard the vacant spaces in his arrangement or table as equivalent to predictions of new elements for he says, "I foresee some more new elements, but not with the same certitude as before" and then he gives one example, predicting a di-tellurium with an atomic weight of 212.

In the first chapter of the second volume of his Principles of Chemistry, Mendeléeff gave much that bears upon the history of the Periodic Law.

This theory is based upon the existence of an attracting and a repelling form of matter and the rotation of the atoms. It is enunciated in opposition to the kinetic theory and is intended to explain all physical phenomena. The theory is brought to bear upon the nature of the ultimate particles of the chemical elements. These are called primary atoms.

From the fact that many of the atomic weights approach whole numbers, that is, are integral multiples of hydrogen, it is assumed that these primary atoms are made up of a limited number of equally small primal atoms. Bühler then discusses the form of one of these primary atoms, supposing it to be made up of ether-atoms and certain ponderable atoms, whose nature is not made clear. The ground form of the primal atom is octahedral and it is made up of ether and the ponderable matter in the proportion of 1 to  $4\frac{1}{3}$ . Covering these atoms there is an ether envelope which lies very closely upon the surface of the atom. These primary atoms are subject to a rotation.

The attraction of two neighboring atoms, the mutual influence of rotating atoms, and other points connected with them are discussed fully and with the aid of mathematics. The theory is extended to the heavenly bodies.

## CHAPTER VIII.

THE DEVELOPMENT FROM 1890 TO 1895.

may be said to begin with a controversy over the proper standard for the atomic weights. The uncertainty as to the oxygen-hydrogen ratio gave rise to this discussion. With each fresh revision of the ratio, giving a new value for oxygen, a great many of the atomic weights of the other elements would require re-calculation, so long as hydrogen, equal to unity, was taken as the standard. The discussion was opened, almost simultaneously, by independent papers by Brauner (178, 190) and Venable (179) and it was joined in by Ostwald (191), Noyes (197), and by Meyer and Seubert, (189) the latter two alone taking up the defense of the old standard hydrogen.

The practical result of the controversy has been the adoption of oxygen as the standard with an atomic weight of sixteen, thus avoiding a fluctuating value for the element most used in determining the ratios of the others.

153. Kronberg's Hypothesis as to the Isomorphism of the Atoms.—The author claimed to have discovered, in 1883, his "cubiponderalgesetz" as a law of the natural groups of equivalent elements. The law is stated thus: "The cube roots of the atomic weights of elements from the natural groups of equi-valent elements, whose compounds show isomorphism, are simple multiples."

The numbers giving the simple multiples are called "specific atom-factors." This is peculiar to each chemical element. To explain this law an hypothesis of

"atom-isomorphism" is formulated, namely, that the atoms of different elements from the natural groups of equivalent elements whose compounds show isomorphism are themselves of geometrically like form and are distinguished mainly by their relative size, which increases in ratios of simple multiples and which only the specific nature of the element, besides the geometric form, determines.

There would then be no necessity for the supposition of a special chemical force. The atomic weight and the universal gravitation of matter suffice to account for all phenomena. The new law and hypothesis, the author says, afford to physics and chemistry two mathematical ideas, in the place of misty notions implied in the so-called natural groups of the elements and in the specific nature of an element, ideas which shall give a mathematical explanation and mode of calculation for all physical characteristics of matter.

His table is here repeated so as to make the law somewhat clearer.

TABLE FOR THE "CUBIPONDERALGESETZ."

| Groups of equi-valent ele-        | Atomic         | Cubic        | Multiples or atom factors. |                                 |
|-----------------------------------|----------------|--------------|----------------------------|---------------------------------|
| ments with isomorphous compounds. | weights.       | roots.       | Theory.                    | Calculated up-<br>ou constants. |
| 2.—Valent Calcium                 | 39.91          | 3.42         | 4                          | 3.42:4 -= 0.86                  |
| alk. salts. Barium                | 87.3<br>136.86 | 4·44<br>5·15 | 5                          | 4.44:5 = 0.89<br>5.15:6 = 0.86  |
| 4.—Valent Carbon                  | 11.97          | 2.29         | 3                          | 2.29:3=0.76                     |
| carbon Silicon                    | 28.0           | 3.04         | 4                          | 3.04:4=0.76                     |
| silicon Titauium                  | 50.25          | 3.69         | 4<br>5<br>6                | 3.69:5 = 0.74                   |
| group. Zirconium                  | 90.4           | 4.49         |                            | 4.49:6=0.75                     |
| Thorium                           | 231.96         | 6.14         | 8                          | 6.14:8 = 0.77                   |
| 3 and 5Valent Arsenic             | 74.9           | 4.22         | 5                          | 4.22:5=0.84                     |
| arcenia aroun ) Autimony          | 119.6          | 4+93         | 6                          | 4.93:6 = 0.82                   |
| arsenic group. (Bismuth           | 207.5          | 5.92         | 7                          | 5.92:7 = 0.85                   |
| 2 and 6Valent Molybdenum          | 95•9           | 4.58         | 4                          | 4.58:4=1.14                     |
| group. (Tungsten                  | 183.6          | 5.68         | 5                          | 5.68:5=1.14                     |
| 2 and 4.—Valent (Sulphur          | 31.98          | 3.17         | 3                          | 3.17:3=1.06                     |
| culphus group   Seleulum          | 78.87          | 4.29         | 4                          | 4.29:4 = 1.07                   |
| sulphin group. (Tellurium         | 127.7          | 5.04         | 5                          | 5.04:5=1.01                     |
| IValent (Chlorine                 | 35.37          | 3.28         | 4                          | 3.28:4=0.82                     |
| halogen Bromine                   | 79.76          | 4.31         | 5                          | 4.31:5=0.86                     |
| group. (Iodine                    | 126.51         | 5.02         | 6                          | 5.02;6=0.84                     |
|                                   |                |              |                            |                                 |

## The first paper by this author appeared in 1888 and is quoted by Mendeléeff in his Faraday Lecture in 1889 and in the second volume of his Principles of Chemistry The following abstract is taken from a later publication (193) of Tchitcherine in the year 1890, presumably more complete than the earlier one which has not been

154. A System of the Elements by Tchitcherine.—

accessible to the compiler.

Taking the Periodic Law as a starting point, as given in the table of Mendeléeff, it is first pointed out that with the increase in atomic weights, the elements pass through periods of condensation and rarefaction. Each period of condensation commences with an alkali and each period of rarefaction terminates with the same. Two consecutive periods, one of condensation and one of rarefaction, constitute a great period or cycle. The lengths of these periods, *i. e.*, the differences between the first and the last atomic weight, are not equal. Thus the first (Li-Na) is 16, but the third (K-Rb) is 46 and the fourth (Rb-Cs) is 47.

With the increase of atomic weight he holds that volume and density also increase. Further, the atom is supposed to be made up of certain units of matter and it is maintained that the increase of density, with increase of atomic weight, shows that so long as the total volume of the atom increases, the volume of each unit of matter which enters into its composition diminishes. The action, or the mutual attraction of the particles results in drawing them nearer, and this makes the volume of each unit diminish in spite of the increase of the total volume.

This diminution of the volume of an atom is called the "loss" (la perte.) By mathematical reasoning, applied especially to the group of the alkalies, since "the numerical coincidences can not be chance" two laws are deduced:

- 1. The losses are proportional to the masses.
- 2. They are inversely proportional to whatever it may be required to determine.

The first is called the law of proportionality of the losses; the second is the law of the diminution of the losses.

This law can be formulated as follows:

$$\frac{p'}{m'} = \frac{p_2}{m_2} = \frac{p_3}{m_3} = f.$$

The last term is a constant, which expresses the bond, or the reciprocal action of each unit with each unit, or, that which may be called the force of cohesion, or molecular attraction, of the atom. In multiplying this value by the mass m, the bond of each unit, with all the others, is gotten. The strength of this bond is measured by the drawing together of the particles, that is to say, by the diminution of their volume, or the loss. Hence p = fm. Under these conditions the volume of each unit or the partial volume, as it may be called, for brevity's sake, is expressed by the formula v = 2 - fm, and the total volume of the atom will be  $V = vm = fm^2$ .

If we compose a table on this basis for the entire series of numbers, commencing with the unit, taking the force of cohesion equal to that of lithium and of sodium, i. c.,

o.3/7 or o.0428571, we will have the proportional sizes (amounts) of the losses, the volumes, and lastly of the densities. In this table, the loss will increase in an arithmetical progression, with a differential equal to o.0428571, and the partial volume will diminish in the same dimension until the first decrease is equal to the second and the second to zero. The last term of the progression will be given consequently by the equation

2-fm = 0, or  $m = \frac{2}{f}$ . If f = 0.0428571, the last term of the progression will be  $46\frac{2}{3}$ , a very remarkable number in the system of the chemical elements, since it is equal to a great period, that is, the distance between

potassium and rubidium, etc.

Further, Tchitcherine discusses the nature of the atoms. The periphery of an atom is taken to be the exterior limit of the matter contained in it—the surface of a sphere, a ring, or simply the orbit of a body revolving around the central mass. The correspondence of the central mass to that of the periphery has its bearing then upon the observed facts and laws. This idea is illustrated by the relation and interaction of the earth, a central mass and the moon, a peripheric mass.

All of the chemical elements take the form of a complete and rational system following and determined by one single formula  $kp = \frac{mx}{z}$ . Here k is a coefficient which must be determined, m designates the total mass, i.e., atomic weight, x the central mass, z that of the periphery. Experiments give us for each atom the value of p = fm. Of these two factors m indicates the proportional value of the mass and f the relation of the center to the periphery. In accordance with this the formula becomes  $kf = \frac{x}{z}$ . If m = x + z, the two unknowns are determined

by it, but if, besides the central mass and the periphery, there is a neutral zone and m = x + y + z, then it is necessary to know either x or z.

In the alkali group lithium is taken as the central mass. The calculation gives for Na: x = 7, z = 16; for K: x = 7, z = 32; for Rb: x = 7, y = 32, z = 46; for Cs: x = 7, y = 64, z = 62.

The atoms appear as analogues of the solar system, with a central mass and bodies revolving around it.

155. Sutherland's New Periodic Property of the Elements (194).—In solids, the molecules may be assumed to vibrate about a mean position, and, at some characteristic temperature, each solid may be said to have a period of vibration characteristic of its molecule. The most likely temperature for which this would be the case would be the melting point, when the vibratory motion of the molecule just breaks down. Suppose a molecule of mass M and mean specific heat C, heated up from rest at absolute zero to its melting point T. It receives heat MCT proportional to its kinetic energy  $\frac{1}{2}Mv^2$ , where v is the velocity of the molecule at the melting point. By Dulong and Petit's law, MC is approximately constant for the elements, so that v is proportional to  $\sqrt{\frac{T}{M}}$ . Knowing thus the velocity of vibration from its length L, its time, or period  $\frac{L}{2}$ , is obtainable. Let d be the density of the substance, then  $\frac{M}{d}$  represents the volume occupied by the molecule: and if a is the mean coefficient of linear expansion of the substance between absolute zero and T, then  $aT\left(\frac{M}{d}\right)^{\frac{1}{3}}$  represents the increase in the linear dimensions of the space occupied by a molecule when heated from zero to T, and therefore

a molecule when heated from zero to T, and therefore represents the length, or amplitude, of the vibration just as it is going to leave the vibratory state characteristic of the solid. Hence the periodic time p of the molecule at the melting point is proportional to

 $aT \left(Md\right)^{\frac{1}{3}} \sqrt{\frac{MCT}{M}}$ . The value of a is unknown for any

elements, but the author has found an empirical equation by means of which it may be determined, namely,  $aTM^{\frac{1}{6}}$  = const., the constant being about 0.045 for all metals except antimony, bismuth and tin. Substituting this value and dropping all constants from the formula, p

becomes proportional to  $\left(\frac{M}{d}\right)^{\frac{1}{3}} \frac{M^{\frac{1}{3}}}{\sqrt{T}}$ . Taking M as the

atomic weight, and calculating the period of vibration by the above formula, we get for the lithium family: Li, 0.21; Na, 0.43; K, 0.66; Rb, 0.96; Cs, 1.23; or numbers in the ratio 1, 2, 3, 4, 5, 6, and for the next group, Be, 0.35; Mg, 0.70; Ca, 1.04; Sr, 1.62; Ba, 1.88; or numbers in the ratio 1, 2, 3, 4, 5, and 5.3. Copper and silver have periods 0.21 and 0.30, which are nearly as 2 to 3, and involve the same fundamental constant as the main family; and zinc and cadmium have periods 0.32 and 0.47, in which the same peculiarity occurs. The periods of other elements do not exhibit such a marked relation, but the following series is remarkable: Mn, 0.16; Fe, 0.16; Co, 0.16; Ni, 0.17, Ru, 0.21; Rh, 0.20; Pd, 0.23; Os, 0.23; Ir, 0.25; Pt, 0.27.

The periods of vibration of compounds are also considered, and it is found that p for each molecule is a sum of parts due to each atom in the molecule.

156. Carnelley's Algebraic Expression of the Periodic Law (195). The atomic weights of the elements, arranged according to the periodic law, may be represented by the formula  $A = c \, (m + v^{\frac{1}{x}})$  where A is the

atomic weight, c is a constant, m a member of an arithmetical progression, depending on the series to which the element belongs, and v the maximum valency of the group of which the element is a member. After numerous trials, the best results have been obtained when x=2 and  $m=0,2\frac{1}{2},5,5+3\frac{1}{2},5+2(3\frac{1}{2}),5+3(3\frac{1}{2})$ , etc., for each series respectively, from series II to XII of Mendeleeff's table, so that m is a member of an arithmetical progression in which the common difference is  $3\frac{1}{2}$ , except in the first two terms, where the common difference is  $2\frac{1}{2}$ .

The calculated values for c vary from 6.0 (carbon) to 7.2 (selenium) with a mean value of 6.64. The high values of c occur mainly with elements belonging to the higher groups (namely, V, VI, and VII) whilst low values belong to the lower groups (I, II, and III.) The greatest extremes occur in group IV, Ti and Ge being high, C and Si low. The equation  $A = c (m + \sqrt{v})$  be comes A = c(m + 1) for elements of the first group, so that for potassium  $c(m^4 + 1) = 39$  and for silver  $c(m^7 + 1) = 107.7$ . If x represents the common difference in the arithmetical progression, then  $m^7 = m^4 + x$ . and  $107.7c(m^4 + 1) + 3xc = 39 + 3xc$  from which xc = 22.90. In the same way, by taking different pairs of elements of group I, different values for xc are obtained. the mean of which is 22.85, or "the difference between the atomic weights of any two elements in group I (from series IV upwards), divided by the difference between the number of series to which each element belongs

gives a constant, or  $\frac{B-A}{y-x} = \text{const.} = 22.85$  where x and y are the numbers of the series to which the elements A and B respectively belong." The constant 22.85 is very nearly identical with the atomic weight of sodium (22.99). Atomic weights calculated from the equation  $A = c \left( m + \sqrt{v} \right)$  agree more closely with the observed values than do those determined by Dulong and Petit's law. Specific volumes calculated from the volumes so obtained agree well with the usual values. The greatest discrepancies occur at the end of series IV, V, and VII, and at the begining of series XI.

In the equation A = c  $(m + \sqrt{v})$ , the constant c has a mean value of 6.6, which suggests the constant 6.4 of Dulong and Petit's law. If c represents the atomic heat, then atomic weight = atomic heat  $\times$   $(m + \sqrt{v})$  = atomic weight  $\times$  specific heat  $\times$   $(m + \sqrt{v})$ , or t = specific heat  $\times$   $(m + \sqrt{v})$  whence specific heat =  $\frac{t}{m + \sqrt{v}}$ . Specific heats, calculated in this way, agree closely with the observed values, especially if specific heats at high temperatures be taken, since in this case the constant 6.4 of Dulong and Petit's law approximates to 6.6.

The value m in the equation A = c  $(m + \sqrt{v})$  is the member of an arithmetical progression, and is a whole number for the even series and a number and a half for

the odd series, in this way b corresponding with the well-known difference between the series. Again, the common difference is  $2\frac{1}{2}$  for the first three members, but is  $3\frac{1}{2}$  afterwards. This accords with Mendeléeff's statement, that the second and third series are more or less exceptional.

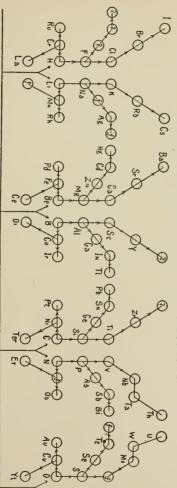
157. Wendt on the Evolution of the Elements .-(201). The natural system of the elements is looked upon as giving, as the first periodicity, seven rows of three elements each, as for instance Li, Na, and K, which bear the closest relationship to one another. This is adduced as a parallelism to the three physical states of matter, and, through analogy, as an argument for the evolution of the elements. It is not to be looked upon as purely molecular nor atomic, but as a change of physical state on the part of like atoms, in accord with the laws for changes of the state of molecules. These changes of state belong not merely to the first, called by the author, stem-elements, but the first  $3 \times 7$  elements have the same capacity for change. Therefore the law runs thus; out of the seven stem-elements two rows of seven elements each were gradually evolved and further from each of the 3 × 7 elements another row sprang.

The elements are arranged into various groups and num-

bered according to the order of their evolution I, II, III, Ia, IIa, IIIa, etc. The reasons for thus arranging certain of the elements, as H, Cr, etc. are discussed at length. There are, as may be seen by reference to the table, many variations from the table of Mendeléeff. Furthermore this system does not show rows of unknown elements. It shows at the most II  $\times$  7 + 2 = 79, at the least 74, or a mean of 77.

The claims made are, that the law on which the scheme is based is the only possible explanation for the connection between the groups and the series of elements. Again, that by it the so-called double periodicity and also the connection between the various parts of the groups are explained. Thirdly the iron, platinum and cerium groups find their positions and explanations. In the fourth place the Kant-Laplace nebular hypothesis, so generally accepted, demands the evolution of the solar system. The astro-physics shows the evolution of the celestial bodies and at the same time of the elements by the gradual aggregation or growth of the same—undoubtedly after their introduction.

The existence of three elements on some celestial bodies and of eighty on others, according to density, would be without explanation were not the elements the result of evolution. The periodicity of the maxima and minima of the sun-spots, in connection with the appearance of the spots in distinct localities only, and the difference of the prominences, seem to point to a continual formation of elements. The presence of the gas D, less dense than hydrogen, upon the sun seems to mean



WENDT'S GENERATION-TREE OF THE ELEMENTS.

that in the cooling of the earth such a gas would be condensed and hence could not exist upon it.

Evolution can not be restricted to organic life since chemistry has shown that the special power or energy called vital force does not exist. With regard to the formation of the seven fundamental elements the author seems most inclined to adopt the views of Grünwald. At any rate they are composed of primal matter. The benefits to be derived from the table he sets forth under thirteen different headings.

His diagram, illustrating his ideas as to the relationship and generation of the elements, may be examined and the similarity of his conceptions to Preyer and others will be seen.

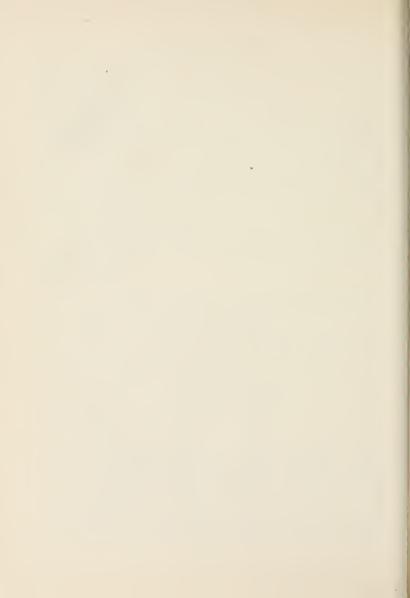
158. A Tabular Expression of the Periodic Relations by Bassett.—The author first (202) mentions some anomalies in the table of Mendeléeff, as for instance, "the great blank space in the fifth column with no indication of the existence of any metals between silver and gold downwards. Again Yb, one of the least basic earths, follows La the most powerfully basic of all. Also Di, with strongly basic oxide, separates Nb and Ta, etc."

The arrangement which he suggests, as meeting these difficulties, "simply amounts to an alteration in the position of Mendeléeff's ninth group and the addition of one interperiodic group." The author describes his table as follows:

"If we cut a strip of paper on which the table has been written and roll it round a cylinder whose circum-

## BASSETT'S TABLE.

|           |                |            |          |              |          | 133<br>137<br>138.2<br>140.2<br>7140.8 | 226 ?<br>?<br>?<br>Th 232.6<br>? |
|-----------|----------------|------------|----------|--------------|----------|--|----------------------------------|
|           |                |            |          |              | Pdy      | 143.6                                  | U 239.6<br>241?                  |
|           |                |            |          |              | Sm       | 150                                    | ;<br>;                           |
|           |                |            |          |              | _        | 154 ?                                  | 248 ?                            |
|           |                |            |          |              | Tb<br>Ho | 159.5<br>162<br>?                      | ;<br>;<br>;                      |
|           |                |            |          |              | Er       | 166.3<br>169 ?                         | ?<br>263?                        |
|           |                |            |          |              |          | 170.4                                  |                                  |
|           |                |            | n.i      | 0.4          | Yb       | 173                                    |                                  |
|           |                | 39.1<br>40 | Rb<br>Sr | 85.5<br>87.6 |          | 174?                                   |                                  |
|           | Sc             | 44         | Y        | 89.1         |          | ?                                      |                                  |
|           | Ti             | 48         | Zr       | 90.6         |          | ?                                      |                                  |
|           | V              | 51.4       | Nb       | 94           | Ta       | 182.6                                  |                                  |
|           | Cr<br>Mn       | 52.1<br>55 | Мо       | 96<br>100 ?  | W        | 184<br>189 ?                           |                                  |
|           | Fe             | 56         | Ru       | 101.6        | Os       | 191.7                                  |                                  |
|           |                | 58.7<br>59 | Rh<br>Pd | 103.5        | Ir<br>Pt | 193.1                                  |                                  |
|           | 23 Cu          | 63.4       | Ag       | 107.9        | Au       | 197.3                                  |                                  |
| Be 9 Mg 2 |                | 65.3       | Cd       | 112          | Hg       | 200                                    |                                  |
|           | 7 Ga<br>8.4 Ge | 69<br>72.3 | In<br>Sn | 113.7        | T1<br>Pb | 204.2<br>207                           |                                  |
|           | I As           | 72·3<br>75 | Sb       | 119          | Bi       | 208.9                                  |                                  |
| O 16 S 3  | 32.1 Se        | 79         | Te       | 125          |          | ?                                      |                                  |
| F 19 Cl 3 | 35.5 Br        | 80         | I        | 126.9        |          | 216?                                   |                                  |
|           |                | (To face   | p. 24    | 16.)         |          |  |                                  |



ference is equal to ten of the vertical spaces, beginning at the bottom, we produce a series of derived tables of considerable interest. The first of these is simply the lowest portion of the primary table as it stands. It will be seen that the elements in the three lower lines show very complete analogies, and a regular gradation in properties from left to right, while in the four upper lines this is by no means so clearly perceived.

"The second fold of the paper round the cylinder covers up all but the two left-hand small periods and gives rise to the following:

| Li | Na | K                      | Rb | ?  |
|----|----|------------------------|----|----|
| Be | Mg | Ca                     | Sr | ?  |
| В  | Al | Se                     | Y  | ?  |
| C  | Si | Ti                     | Zr | ?  |
| N  | P  | V                      | Nb | Ta |
| 0  | S  | Cr                     | Mo | W  |
| F  | C1 | $\mathbf{M}\mathbf{n}$ | ?  | ?  |

"Na is removed from its anomalous place by Cu; Mg, Al and Si also find more congenial neighbors, and so on. By a third fold of the paper the last column above is covered and a new one containing Tb, Ho, and Er is produced. The last fold of the paper covers this up and gives finally the column Cs, Ba, La, Ce, etc. and another with Th and Ur. This gives alkalies, etc. complete and is derived from the first table by successive upward shifts of the first and second pairs of groups or periods."

The author emphasized the importance of the atomic volumes in the arrangement of the periods, though the atomic weights are regarded as of prime importance.

159. Wilde on the Origin of the Elements.—The preface to this paper (203) contains a criticism of the system of Mendeléeff with especial reference to the idea of periodicity. "From the numerous discrepancies which present themselves in the classification of the elements when arranged in the regular order of their atomic weights, it will be obvious that the idea of recurring properties or periodic functions, in terms of the vertical series of Newlands or the horizontal series of Mendeléeff, has no more relation to chemical science than the law of the increase of population, or the laws of variation and inheritance in organic species." The author compares the nebular theory and its condensations with supposed elementary condensations, giving tables of numerical relations among the planetary distances and also between the atomic weights. He gives several tables in illustration of this, thus:

## TABLE II.

0 . 0 . 7 = Li = 7  
1 
$$\times$$
 23 - 0 = Na = 23  
2  $\times$  23 - 7 = K = 39  
3  $\times$  23 - 7 = Cu = 62  
4  $\times$  23 - 7 = Rb = 85  
5  $\times$  23 - 7 = Ag = 108  
6  $\times$  23 - 7 = Cs = 131  
7  $\times$  23 - 7 = 154  
8  $\times$  23 - 7 = 177  
9  $\times$  23 - 7 = Hg = 200

A similar table is given for the Be group with I  $(2, 3, \text{ etc.}) \times 24-8$ ; and another for the elements C, Al, Yt, In, E, Tl, and Th, with I  $(2, 3, \text{ etc.}) \times 27-12$ .

He gives as further relations "observable between inter-planetary voids and atomic condensations;"

- 1. The regular geometric series of the planetary distances commences at the second member of the system, and the regular arithmetical series of atomic weights commences at the second and corresponding member of each series.
- 2. As the atomic weight of the second element in each series is half the sum of the atomic weights of the first and third elements, so is the distance of the second member of the solar system an arithmetical mean, or half the sum of distances of the first and third members.
- 3. The atomic weight of the fourth member, in each series of elements, is equal to the sum of the atomic weights of the second and third and the distance of the fourth member of the solar system is also equal, within a unit, to the sum of the distances of the second and third members.
- 4. As the smallest planetary distance is a constant function of the distances of the outer planetary bodies, so is the least atomic weight in each series a similar function of all the higher members of the series to which it belongs.

Other relations are pointed out but enough has been given to show their nature. Following Prout, he assumed "that hydrogen is the ponderable base of all elementary species and, further, that it is probable that this element itself, as further maintained by Prout, may have been evolved from an ethereal substance of much greater tenuity."

In his hypothesis he assumed, (1) that a mass of hydrogen of a curvilinear form, acquired a motion of rotation about a central point which caused it to take a spiral or convolute form. (2) As each successive spiral or convolution was formed, the particles of hydrogen combined with themselves as far as the septenary combination, constitute the type of each series of elements, the number of types or series being equal to the number of convolutions of the rotating gas. (3) That on a further condensation of the elementary matter a transition from the spiral to the annular form occurred, during which, or after which, the series under each type was generated in concentric zones, and in the order of their atomic weights, until the highest member of each species was formed. (4) That as the elementary vapors began to condense or assume the liquid form their regular stratification would be disturbed by eruptions of the imprisoned vapors from the interior of the restating This disturbance would be further augmented by the subsequent combination of the negative with the positive and also by the various solubilities of their newly formed compounds.

In his annexed table are arranged all the known elements in natural series, wherein gaps appear, as in Tables II. and III., which indicate the existence of missing elements. The atomic weights of other elements which have not been sufficiently investigated are also determined. If the theory of the evolution of elementary substances from hydrogen be correct, the numbers representing the atomic weights also represent the number

of the particles of hydrogen from which the elements were formed.

In a later paper the author reiterates his views as to Prout's Hypothesis and vigorously criticises Mendeléeff and the idea of periodicity.

160. New Numerical Relations by Adkins.—According to this paper (207) all of the atomic weights can be formed from those of the first four elements: Li, 7; Be, 9; B, 11; C, 12. They are formed in regular sequence by taking a "basic number" which is either an alkali or an alkaline earth and adding a regular sequence of the atomic weights: a small anomalous group is the only exception, together with a duplication of 12 in magnesium.

Anomalous Group, Alternate Alkali and Earth Base.

Explanations are offered of the position of Mg and Na; Mg is made up of two elements 12 and 12 and Na of three, 7, 9, and 7. Chlorine is said to be of compound

character, 
$$35 + 36 = \frac{71}{2} = 35.5$$
.

It is scarcely necessary to give more of the sequences arranged by this author. Suffice it to say that they are more strained and complicated as the atomic weights increase. Finally, he says "the remaining groups are so incomplete that it is difficult to follow further on this system but they can be developed in another way." There is no discussion as to the meaning of these groups nor of their chemical relations, nor are any reasons given for the assumption of "basic numbers" and of sequences, and the reader is unfortunately left in the dark as to the object of the entire calculation.

Meusel (208) sought to find in the differences between the atomic weights of the members of the different series a revelation of the composition of the elements. These point to a common factor. One cannot longer think of the chemical elements as simple bodies, still it is difficult to deduce this common factor. The best method seemed to the author to be to take the differences of the first members of the different series, that is, Li, Be, B, C, N, O, and F.

```
Li 7.01 = 3.99 + 3.02

Be 9.08 = 3(3.02) + 0.02

B 10.09 = 2(3.99) + 3.02

C 11.97 = 3(3.99)

N 14.01 = 2(3.99) + 2(3.02) - 0.01

O 15.96 = 4(3.99)

F 19.06 = 3.99 + 5(3.02) - 0.03
```

A table is given showing that all the atomic weights can be built up out of these two factors, 3.99 and 3.02

with small plus and minus differences. These differences are regarded rather as giving proof that the elements are made up of these two factors, than otherwise, since the atomic weights are not accurately known and absolute accord is not to be expected. That one of the elements, hydrogen, has an atomic weight less than either of the factors may be explained on the ground that all of them have like origin, or consisting of like primal matter and show similarity of constitution.

"The next task was to discover the common origin of the three magnitudes 1.00, 3.99, and 3.02 and if possible to get a clear idea of the space relations of these weight magnitudes. For the solution of the problem the simplest system was adopted in accord with moving atoms. The simplest forms in space determined by four given points are the tetrahedron and the sphere. The four angles of a tetrahedron replaced by four atoms form the simplest system reconcilable with the movement of the atoms. This tetrahedron is taken as the starting point. An increase of this tetrahedron by a similar one would give seven points and upon forms in space of four and seven points the following combination forms can be gotten: 10..13....100.....133.....199...202..... 334, etc. If these points represent atoms of primal matter we will have bodies formed by tetrahedral series of primal matter.

"But we can not stop with this representation. Series in right lines would have no limit and lead to endless forms and this would conflict with our present knowledge of matter. Considerations of gravity and motion make circular series of the spherical form more probable.

"If thirty-three tetrahedra are arranged, with one common point for each pair, in a half circle, one end will be formed by the figure  $+\frac{0}{2}$  and the other by  $-\frac{0}{2}$ . The final tetrahedron corresponds to the first, turned through 180°. The simplest system of such uniformly moving bodies, consisting of 100 atoms, would be two such half circles. Thus each half circle would be an atom of hydrogen, and the complete circle a molecule. A larger molecule of this body has never been observed and the creative thought has used this for building all the so-called chemical elements.

"Let us test this supposition upon the magnitudes 3.99 and 3.02. In condensing two half circles of atoms of hydrogen, one atom of the primal matter forms the point of union, thus the two will consist of 199 such atoms." To get this number, 3.99, the author unites two such figures, 1.99, plus a binding atom, and, for the magnitude, 3.02, it is one figure 1.99 and one half circle bound together by four atoms.

"The space relations of these magnitudes can be fixed by the specific gravity, or atomic volume, of the chemical elements. Each of these magnitudes has two sizes. For 3.99 we see in carbon the size 1.2 with sp. gr. 3.324, while in lithium the size is 6.76 with a sp. gr. 0.5902. The magnitude 3.02 corresponds in beryllium to the size 1.63 with a sp. gr. of 1.853, whilst in lithium they are 5.12 and 0.5898, respectively."

On applying this theory to the constitution of the various elements, the author thought that it offered an

explanation of the allotropism of certain of the elements, this being due to molecular rearrangement. As can be easily seen the elements of larger atomic weight give wide choice as to constitution. Thus Cd, 111.7 or 28(3.99)—0.02; or 37(3.02)—0.04; or 22(3.99) + 8(3.02)—0.24; or 25(3.99) + 4(3.02)—0.13.

This theory is further considered in connection with atomic volumes and valence. The author regards the building up of the elements as a building of tetrogen (3.99) and trigen (3.02), in accord with the laws of equilibrium. This same principle is the foundation of chemical combination and of valence. He does not believe in a specific force, chemical energy. Valence depends upon neither atomic volume nor upon atomic weight; it is ordered neither in accordance with the metallic, nor the non-metallic character; it is not subject to the same graded changes as the other properties. Take chlorine, as an example. Towards electropositive hydrogen the atom particles of chlorine so move themselves that only one circle has need of a new equilibrium. Some elements, however, as, for instance, the electropositive oxygen, are capable of so influencing the motion of the atom-particles of chlorine that these seek a new equilibrium.

Meusel laid special stress upon the proof brought to his theory by thermo-chemical data, believing that his theory alone gives these their proper explanation.

162. The Generic System of the Elements by Preyer.
—A table is given by Preyer (206) of the elements arranged in fourteen grades or steps. These steps are

named by "step-numbers," from one to fourteen, giving thus the order of the evolution of the elements.

period of three; 5 is the fourth seven; 6 is the fifth seven; 7 is the second period of three; 8 is the sixth seven; 9 is the seventh seven; 10 is the eighth seven; 11 is the ninth seven; 12 is the third period of three; 13 is the tenth seven; 14 is the eleventh seven.

These correspond to five generations:

These are condensation steps. Thus the second condensation would give rise to the elements of steps 2, 3, and 4, and the fourth to those of 9, 11, 12, 10, and 8, etc. It can be presumed that the elements of steps 14 were formed by condensation from elements 9 and both elements 9 and 11 by condensation from 6 etc.

Combining the five generations with the fourteen condensation grades the following stem-table or generic system is derived.

Three of the eight groups will be here given as illustrating the whole.

|                        | н       | Н            | Н           |  |  |  |
|------------------------|---------|--------------|-------------|--|--|--|
|                        | Li      | Ве           | Во          |  |  |  |
| K                      | Na      | Ca Mg        | Sc Al       |  |  |  |
| Rb                     | Cu      | Sr Fe Zn     | Y Ga        |  |  |  |
| Cs                     | Ag      | Ba Ru Cd     | La In       |  |  |  |
| $\mathbf{D}\mathbf{p}$ | Sm Au   | Yb Os Hg     | Gd T1       |  |  |  |
|                        | valence | even valence | odd valence |  |  |  |

And so other groups are given, springing from C, N, O, and F.

Here we find the various families recognized and included by Mendeléeff in his natural system. Here, however, they are brought into their genetic relationship. Preyer uses a Roman numeral to indicate the generation of the element and the common numeral for the condensation step. The two together will fix the position of any element. Elements belonging to the same condensation step are called the *isotopic* elements; those of the same generation are said to be *stem-related*.

Proofs for the correctness and truth of this arrangement are drawn first from the regularities observed in the differences between the atomic weights. A full table of the differences between the atomic weights of stemrelated and isotopic elements is given. First we have the differences between the first and second generation. This is then divided by the difference between the generation numbers.

$$2-I=I \qquad 3-I=2 \\ I. Na-Li=I\times 16.0 \qquad K-Li=2\times 16.05 \\ II. Mg-Be=I\times 15.3 \qquad Ca-Be=2\times 15.5 \\ 4-I=3 \\ II. Fe-Be=3\times 15.66 \\ IV. Co-C=3\times 15.3 \\ VI. Ni-O=3\times 14.3$$

These differences are determined for all generations. They range from 13.5 to 19.1. The means of any one series range from 14.88 to 18.75. These facts are summed up into a so-called "Law."

If, instead of dividing the differences between the atomic weights by the differences between the gradation numbers, the atomic weights themselves be divided, the quotients given show how much the condensation is from the beginning in the various gradations. These quotients range from 11.52 to 17.3. This he regards as a new means of controlling doubtful atomic weights and of the approximate determination of those of unknown elements.

Finally, it is observed that the arithmetic mean of the atomic weights of each of the fourteen series of isotopic elements is without exception the same as the atomic weight of the elements in the middle column. Thus:

Weight of the elements in the middle column. Thus:  

$$\frac{\text{Li} + \text{Be} + \text{B} + \text{C} + \text{N} + \text{O} + \text{F}}{7} = 12.59 = \text{C} + 0.5.$$

$$\frac{\text{Na} + \text{Mg} + \text{Al} + \text{Si} + \text{P} + \text{S} + \text{Cl}}{7} = 28.75 = \text{Si} + 0.42.$$

The specific gravities, atomic volumes, specific heats, atomic heats, valence, electro-chemical, and other properties are all tabulated, and the numerical relationships between these are adduced as evidence in favor of this attempt at a genesis of the elements.

163. Wislicenus on the Nature of Matter.—Wislicenus (209) has given an historical review of the development of the atomistic idea and theories. No new theories are advanced. The Proutian hypothesis is looked upon

as fully disproved. "Whatever theory as to the nature of matter may be finally accepted it must be based upon chemical and physical research and must be atomistic in nature."

criticizes some points in the table of Mendeléeff, especially his arrangement of the "typical elements" or as some have called them the "anomalous elements." Mendeléeff seems to have arranged them largely for symmetry, in the author's opinion. He objects to Meyer's diagram where the abscissae are atomic weights and the ordinates are atomic volumes, because, though the regular variation of the ordinates is very striking, the lines joining their summits do not form very regular curves. This might result from inexact data or more probably from lack of corrections for temperatures as compared with melting points.

His diagram is constructed in much the same manner as L. Meyer's, but the periodic variations of some other physical constants of the elements, that are marked by even greater regularity than are the atomic volumes, are plotted upon it. The two constants used are deduced from the atomic weights, the relative density, and the specific heat. These constants are called the volume-heats and the volume-atoms.

The volume-heats are the quantities of heat required to raise equal volumes of the elements, in the solid condition, through equal temperatures, whilst the volumeatoms give the relative numbers of atoms in equal volumes. The relative density changes periodically with

DEELEY'S ARRANGEMENT—CLASSES OF OXIDES.

|   |     |       |       | Se                                       | ries   | s of    | ele    | mer      | ıts.                 |         |               |    |      |
|---|-----|-------|-------|--|--------|---------|--------|----------|----------------------|---------|---------------|----|------|
| R <sub>2</sub> O <sub>1</sub> .   |     | !     | →<br> | S. S | Cu     | Pd → ↓  | Ag     | <b>→</b> | ۸.                   | Pt → ↓  | Au            | ۸. | XI   |
| R <sub>2</sub> O <sub>2</sub> .   | Be  | ı     | Mg    | ↓ Mn →                                   | Zn     | ↓ Rh →  | Cd     | ۸.       | ۸.                   | Ir 🕂    | Hg            | ۸. | VIII |
| R <sub>2</sub> O <sub>3</sub> .   | B   | 1     | A1.   | Fe → ←                                   | Ga     | ↓Ru → ↓ | In     | → ~:     | ۸.                   | → ↑ so  | Tl            | ۸. | VII  |
| R <sub>2</sub> O <sub>4</sub> . R <sub>2</sub> O <sub>3</sub> .                                 | C   |       | Si    | Cr ↓ ↓                                   | † Ge   | † Wo ↓  | dS †   | ٠.       | ۸.                   | † M     | d <b>T</b> Pb | n  | VI   |
|   | Z   | →<br> | Ŋ     | → ^                                      | ↓ As   | → qN →  | † qs † | ~÷       | <i>م</i> ،           | Ta 👃    | ↓ Bi          | ۸. | Λ    |
| R2O4.   | 0   | →<br> | S     | Ti                                       | † Se ← | Zr 👃    | ↓ Te ↓ | † Ce ↑   | <ul><li>~.</li></ul> | →<br>~. | <             | Th | IV   |
| R <sub>2</sub> O <sub>3</sub> . R <sub>2</sub> O <sub>4</sub> . R <sub>2</sub> O <sub>3</sub> . | H   | →<br> | ひ     | sc t                                     | ↓ Br   | ↑ A     | 1 +    | La 👃     | ~·<br>→              | ↑ qX    | ~.<br>→       | ۸. | III  |
| R <sub>2</sub> O <sub>2</sub> .   | 0-1 | 1     | 1     | Ca                                       | <br>   | Sr      | <br>   | Ba       | <br> <br>→           | ۸.      | <br>          | ۸. | II   |
| R <sub>2</sub> O <sub>1</sub> .   | H   | Na    | <br>  | K  | <br>   | Rb      | <br>   | Cs       | <br> <br>            | ۸.      | <br>→         | ۸. | I    |
|   | 2a  | Ia    | 71    | 3  | 4      | S       | 9      | 7        | oo.                  | 6       | IO            | II |      |

Distribution in classes, series and groups. The grouping of the elements is indicated by arrows.

increasing atomic weight. The specific heat does not. Besides increasing rapidly with increasing atomic weight, the relative density is a markedly periodic value. To illustrate this periodicity the regular increase of density must be eliminated from the ordinates. This is accomplished by making them volume-atoms. The constants have been determined for the elements in the solid state and, when allotropic modifications exist, for its most stable form. The following equations give the various relationships.

 $Volume-Atoms = \frac{Relative Density}{Atomic Weight}.$ 

Volume-Heats = Relative Density × Specific Heat.

Atomic Heat =  $\frac{\text{Volume-Heat}}{\text{Volume-Atoms}}$ .

In the diagram given by Deeley, the abscissae are the atomic weights, and the ordinates are volume-heats and volume-atoms. The volume-atoms, to enable a clear comparison to be made, have been multiplied by 6.1, the mean atomic heat of Dulong and Petit. Where the volume-heats and volume-atoms are almost identical, the spots have been surrounded by circles.

Diagram 1 includes the first seven elements in the table of Mendeléeff, 2 the second seven, 3 the third seven, etc.

With the exception of certain peculiar features, which are shown by the elements of lower atomic weight than aluminium, the elements fall naturally into eleven series. Assecond table presents these more completely (page 260).

165. Palmer's Views as to the Nature of the Elements.

—During the years 1890–1893 several papers were pub-

lished by Palmer (211) bearing upon the nature of the chemical elements. In the first paper attention was drawn to the facts that the atomic weights are the chief constants of the chemical elements; that they follow each other in a fairly regular progression; that in this progression the elements beyond hydrogen arrange themselves naturally in series; that the natural grouping is best shown when the elements are arranged in series, whether long or short, which begin with an alkali and end with a halogen; that these series, either long or short, have a similar progressive variation in (a) physical properties (b) chemical properties, and (c) in chemico-physical properties. From these facts the inference was drawn that the elements, so-called, are made up of two sub-elements or ingredients, viz., kalidium (Kd) and oxidium (Od).

The hypothesis as to the existence of these sub-elements is then examined from several standpoints. The elements may have been formed by the addition method as Li = Kd; Be = Kd + Od;  $\text{B} = \text{Kd} + \text{Od}_2$ , etc. Or they may have been formed by the substitution method:  $\text{Li} = \text{Kd}_6$ ;  $\text{Be} = \text{Kd}_5 + \text{Od}$ ;  $\text{Be} = \text{Kd}_4 + \text{Od}_2$ ;  $\text{C} = \text{Kd}_4 + \text{Od}_3$ , etc.

The addition method is discarded since the progression is not a regular one. In the same way, considering the simpler substitution method, the numerical results are by no means satisfactory. This, he says, does not dispose of the question of the composition of the elements in terms of oxidium and kalidium, but only points to another mode, and probably an excessively fine degree

of subdivision of the atom in terms of sub-atoms; i.e., that the atom is made up of parts excessively minute as compared with the atom.

The hypothesis that hydrogen is the proximate ingredient of the elements is discredited because the atomic weights have not been found to be exact multiples of unity; because hydrogen is inherently basic and, while it might be looked upon as the prototype of basic-forming elements, it cannot be of the acid-forming; and lastly, hydrogen is probably part of a complete independent series as yet unknown. He thinks one such series possible but not two. The supposed properties of the last element of this series, or pre-fluorine, are discussed. As to the generic kalidium and oxidium, he states that they are not necessarily concrete, isolable, varieties of matter but they represent the embodiment of those antithetic properties which are synonymous respectively with basiferous and acidiferous properties. This is, as he points out, a return to the Greek idea of element or principle. An hypothesis as to the genesis or evolution of the elements is then advanced as an explanation of the various facts observed in connection with the atomic weights. This presents an analogy to the nebular hy-The various theories advanced by Palmer bear many points of resemblence to those of Zängerle, Crookes and other writers already cited.

The author criticizes the classification of Mendeléeff in detail, on the ground of the forced analogies between certain elements.

He gives a new arrangement into "short and long

series." His theory leads him to the supposition that the individual atoms of the same element may differ among themselves as the blades of grass on the lawn. To settle this question he proposes to adopt methods of separation like fractionation. This we have seen suggested by Crookes and others and tried by Despretz. At the close of his last paper he said that a few months would see much light thrown upon this subject by the fractionation of silver upon which he proposed to start. Two years have since elapsed without further report from him.

- by the Aid of the Periodic System.—When the German Society, according to its custom of inviting some distinguished specialist to lecture before it, extended its invitation to Lothar Meyer, he devoted (210) the opportunity him to an earnest argument and appeal in favor of afforded the immediate and complete introduction of the periodic system and tables into the regular courses of instruction in inorganic chemistry. He pointed out the necessity for this if the system was a true one and the great saving in time which it rendered possible, as well as the clearness of order and treatment gained. It means to inorganic chemistry what the introduction of compound radicals and homologous series meant to organic chemistry and will accomplish as much for it.
- 167. Hinrichs on the True Atomic Weights.—Hinrichs has reiterated in this volume (217) his ideas about the pantogen atoms and the composition of the elements, expressed in his earlier publications. He is convinced

that in the determination of the atomic weights the analytical ratios found depend upon the amount of the element used in the experiment, and hence that there is a systematic variation in these atomic weights. Some of his criticism upon the methods of calculating the atomic weights, at present in vogue, would seem to be justified. He derives what he styles the true atomic weights by the limit method. This requires the "execution of a true series of determinations, all made under exactly the same conditions, with exactly the same materials, and differing only in the amount of the independent taken, and this amount should vary gradually between the two extremes determined by the possibility of ready handling and exact determinations."

If such a series is plotted over the atomic weight as absciss aand the analytical ratio as ordinate, the latter will determine a parabolic trajectory which has its convexity either turned up or down, and, accordingly, exhibits either a maximum or minimum.

"The individual values determined vary according to a definite law, approaching a definite limit as the quantity of matter operated upon approaches zero; and that this limit gives the true atomic weights on which chemical science is to be built."

The standard unit taken is one twelfth of the atomic weight of carbon, in the form of diamond. Working by his limit method, he regards it as proved "that of nineteen elements examined, all are exact multiples of the hydrogen weight." For other elements new determinations are necessary. In a few cases these weights are multiples

of half the weight of hydrogen. "The unity of matter is the logical and necessary conclusion from this fact."

## 168. Rang's Periodic Arrangement of the Elements.

— The general plan of Rang's table (213) is to arrange the elements in their respective series, so that all the allied elements should come in the same vertical row.

|               |     | RA   | NG'S | PER  | iodio | AR  | RANG         | EMENT    |    |               |                     |
|---------------|-----|------|------|------|-------|-----|--------------|----------|----|---------------|---------------------|
| Va-<br>lence. | I.  | II.  | III. |      | IV.   | v.  | VI.          | VII.     |    | VIII.         |                     |
| I.            | • • | • •  |      |      |       |     |              |          |    |               |                     |
| 2.            | Li  | Be   | В    |      | C     |     | • •          | • •      |    |               |                     |
| 3.            | Na  | Mg   | A1   |      | Si    |     | • •          | • •      |    | • •           | • •                 |
| 4.            | K   | Ca   | Sc   |      | Ti    | V   | Cr           | Mn       | Fe | Ni            | Co                  |
| 5.            | Rb  | Sr ' | Y    |      | Zr    | Nb  | Mo           | • •      | Ru | Rh            | $\operatorname{Pd}$ |
| 6.            | Cs  | Ba   | Di   |      |       | Ta  | W            | • •      | Os | Ir            | Pt                  |
| 7.            | • • | Mn   |      |      | Th    | ٠.  | U            |          |    | • •           | • •                 |
| Group         | 1.  | 2.   | 3.   |      |       |     |              |          |    |               |                     |
|               |     | Ă.   |      |      |       |     |              | 4.<br>В. |    |               |                     |
| Va-           |     |      |      |      |       |     |              |          |    |               |                     |
| lence.        | I.  | 1    | ſ.   | III. |       | IV. | v.           |          |    | VI.           | VII.                |
| I.            | • • | •    | •    | H    |       | • • | • •          |          |    | • •           |                     |
| 2.            | • • | •    | •    | • •  |       | • • | N            |          |    | O             | F                   |
| 3⋅            |     |      | •    |      |       |     | $\mathbf{P}$ |          |    | S             | C1                  |
| 4.            | Cu  | Z    | n    | Ga   | (     | Ge  | As           |          |    | Se            | Br                  |
| 5.            | Ag  | C    | d    | In   | 5     | Sn  | Sb           |          |    | Te            | I                   |
| 6.            | Au  | H    | [g   | Tb   | ]     | 2b  | Bi           |          |    | • •           |                     |
| 7.            |     |      |      |      |       | • • |              |          |    | ••            |                     |
|               |     |      | 5    |      |       |     |              |          |    | - <del></del> | 7                   |
|               |     |      | č    |      |       |     |              |          |    | T)            |                     |

Di here represents all the triads that are between Ba and Ta. H may not be exactly in its true place, still it cannot be very far from it.

The table has been divided into four groups, A, B, C, and D, where, of the end group, A contains the strongest

positive elements, and the other end group D the strongest negative elements. In the center groups B are the elements with high melting points; they are all remarkable for their molecular combinations. At one side of this group are the anhydro-combinations: in the other center group, C, are the heavy metals that have low melting points. If groups A and D be split up vertically in respectively three and two parts, the table presents seven vertical groups, and horizontally seven more or less complete series. Each group in each of the series 2 and 3 are represented by one element. "The octave appears also both horizontally and vertically in the table."

169. A New System of the Elements by Traube.—The fact is pointed out by Traub (215) that certain failings in the system of the elements as given by Mendeléeff, based upon the principle that the properties of the elements are periodic functions of the atomic weights, have been generally recognized. In various instances an element does not receive that place in the system which should belong to it, because of its chemical relationship. In many cases an element presents resemblances to a number of elements in different groups. In the Mendeléeff system only one place can be assigned to it. Finally the very probable hypothesis as to the unity of matter speaks against the probability that the atomic weights alone should decide the properties of the elements.

Thus the author thinks that the older system has too one-sided a principle for its basis. He believes, upon the ground of his researches upon the atomic and molecular volumes of solution, that the space occupied by anatom is as fundamental a constant as its mass (atomic weight). For the atomic volumes at least as simple relations obtain as for the atomic weights. Therefore the law might be written: The properties of the elements are functions of the atomic weights and of the atomic volumes. The elements can be brought into a still more natural system by a consideration of the atomic volumes as well as the atomic weights. The author fails to arrange such a system, however, offering only series of natural families for consideration. In these, the same element, according to valence, finds its place in different series.

The first natural family given is H, Li, Na, Cu (monad), Au (monad), and Hg (monad). The uniting bond here is the equivalence of the atomic volumes, as the atomic weight relations are by no means simple. A branch of the family includes ammonium and the elements sodium, potassium, rubidium, cæsium. The atomic volumes of the four elements differ by about 10 units. The volume of ammonium is equal to the atomic volume of rubidium. Thallium (monad) stands near to potassium. Other groups are discussed in a similar manner. The following advantages are claimed for the system.

- 1. The inequalities of the periodic system are removed.
- 2. Even where no simple atomic weight relationship is shown between nearly related elements, the bond is furnished by the simple relations of the atomic volumes.
- 3. The possibility of change of volume on the part of the atoms, the "Polysterism," stands in close causal con-

nection with the fact that an atom can change its properties and its valence and in consequence must take its place in different families.

With full recognition of the services rendered by the periodic system the author thinks the principle proposed by him a step forward in the satisfactory establishment of the properties of the elements.

170. A Modified Arrangement of the Elements by Venable.—'This paper (222) contains first a criticism of certain points in the ta bleof Mendeléeff. The varying length of the periods; the anomalous place assigned to the triads, or tetrads, Fe, Co, Ni, and Cu, and also to other single elements; the large number of unknown elements which are assigned places in order that certain known elements may fall in the groups to which their other properties would naturally assign them, and similar difficulties are mentioned. Thus there are sixteen elements unknown between cerium and ytterbium; the third great period of seventeen elements contains only four known ones; and the fifth only two; only one of the five great periods is filled out. In the periodic system arranged by Mendeléeff there are sixty-four known elements and thirty-five empty places.

The suggestion is then made that in order to obviate some of these difficulties the idea of periodicity be subordinated at least until it can be fully proved. This would do away with any necessity for periods of seven or seventeen. The really essential parts of the natural system are that the elements form a continuous ascending series, and secondly that the properties are deter-

|        |                   |                     |          | 1               |       | ·Z-        | 48    | Þď          | 88    | Pt-   |    |     |
|--------|-------------------|---------------------|----------|-----------------|-------|------------|-------|-------------|-------|-------|----|-----|
|        |                   | -                   |          |                 |       | -ပိ        | 47    | Rh          | 86    | Ir    |    |     |
|        |                   | -                   |          |                 |       | т-<br>- F- | 46    | I Ru        | 81    | Os    |    |     |
| MH     | $\mathrm{M_2O_7}$ | 压-                  | 16       | -5<br> <br>     | 20 45 |            |       |             |       |       |    |     |
| $MH_2$ | MO <sub>3</sub>   | -   0 -             | 16       |                 | 47    |            | 47    |             |       | _     |    |     |
|        |                   | <br> <br> <br> <br> |          | -               | 50    | As Cr      | 5 44  | SbMo        | 88    | BiW   | 54 | Ür  |
| MH3    | $\mathrm{M_2O_5}$ | <br> -              | 11       | - <sub>24</sub> | 20 44 |            |       |             |       | PbTa  |    |     |
| MH4    | $MO_2$            | ر<br>ا<br>ا         | 16       | Si              | 44    |            |       | Sn Nb       |       |       | 0  |     |
|        |                   | B -                 | 16       | -               | 43 20 | Ga Ti      | 43    | InZr        | 91 5  | TICe  | 96 | -T- |
|        | $\mathrm{M_2O_3}$ | д-                  | <u> </u> | -A-             | 11    | Zn Sc      |       |             |       | HgLa  |    |     |
|        | MO                | Be –                | 15       | Mg              | 16 41 |            |       | -3          | 50 88 | Hg t  |    |     |
|        | 03                | i —2— Be            | 16       | _Na   _Mg       | 40    | Cu Ca      | 45 47 | Ag Sr (     | 88    | Au Ba |    |     |
|        | $M_2O$            | 13                  |          | -Z<br>          | 91    | -14        | 9\$   | $R_{\rm b}$ |       | Cs-   |    |     |

mined by the atomic weights or dependent upon them.

The new table is built up as follows: At the head stand seven group elements, having a difference of about 2 between their atomic weights. These can also be called the "bridge elements" since they show a notable gradation of properties from one to the other and serve as bridges between the different groups. To these are linked, with a difference in atomic weights of 16, seven "typical elements." These elements have the typical properties and characteristics of the group and show a wider divergence from the neighboring groups. From the typical element of each group diverge two sub-groups, generally triads though they may be changed into tetrads or pentads by the discovery of other elements. These show fairly regular increments in the atomic weights. Much stress is laid upon these differences between the atomic weights throughout the entire arrangement. In the first four groups the left or positive series of three is most like the type; in the last three the reverse is true. The left series is more positive and the right more negative. The author does not claim originality for the arrangement as it is partly given in the work of Bayley, and Wendt. Nor is it offered as of special theoretical value, making clear any law of nature as to the genesis of the elements, but rather as a help in systematizing the teaching of chemistry.

171. The Rational Atomic Weights of Thomsen.— Thomsen (219) took as the basis of his research, upon what he styles a remarkable relation between the atomic weights, his recalculation of the atomic weights as given by Stas. When oxygen is taken as sixteen, these all vary more or less from whole numbers. He proposed to multiply these by some common factor, which, without changing their mutual relations, would render it possible to assign a common cause to these deviations from integers. From a consideration of the relation found by Stas to exist between the atomic weights of silver and oxygen, or the silver-oxygen ratio, Thomsen deduced the factor 1.00076. If the atomic weights of the other simple bodies are multiplied by this factor then their differences are very nearly multiples of 0.0120. This would seem to indicate a common cause for the deviations. The graphic method is used to bring out the relation. Making use of this the author calculated what he called the rational atomic weights.

172. A Systematic Grouping of the Elements by Thomsen.—Julius Thomsen (234) has found unsatisfactory the grouping of the elements as given in the tables of Mendeléeff and Meyer. One of the chief difficulties lies in the large number of rare earth metals with closely approximating atomic weights.

He therefore suggests a new grouping, the nature of which can be readily understood from the table appended to his article. It is not necessary to repeat this table here. It is almost identical with the one given by Bayley and afterward used by Carnelley (p. 175). In a private communication the author writes that the work of these authors was entirely unknown to him. In the fifth group a difference appears between the two arrangements. Bayley's fifth group contains nine elements

with greater atomic weight than bismuth. Thomsen limits this group with bismuth as third and last member.

Hydrogen forms the head of Thomsen's table; the remaining elements are divided into three chief groups of which the first contains twice seven elements, the second twice seventeen and the thirdthirty-one. There is perhaps a fourth of thirty-one. Thomsen draws attention to the curious fact that the number of the elements in the several series can be expressed thus:

$$1 + 2.3 + 2.5 + 2.7$$
 or 1, 7, 17, and 31.

The two first groups consist of two series each but the third does not admit of division into series. The table is intended to show the genetic relationship of the elements. The series are arranged from electro-positive to electro-negative. In the transition from the first to the second group each member of the second series is related to two members of the third, one electro-positive and the other electro-negative.

173. Thomsen's Group of Inactive Elements.—Thomsen (233) draws attention to the transition per saltum of Reynolds, the sudden change from negative to positive, which is observed in passing from fluorine to sodium and from chlorine to potassium, etc. If the chemical character of the elements is to be looked upon as a periodic function of the atomic weight then such a function must follow the common laws. One of these is that in the passage from negative to positive values, and vice versa, the transition must be either through zero, and gradual, or through infinity, and sudden. The first case corresponds to the gradual change in electrical

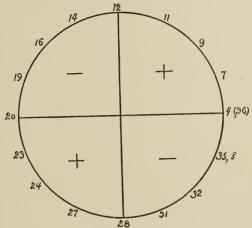
character in a series of the elements in the periodic system; the second to that which takes place in passing from one series to another. This passage, then, must take place through an element whose electrical character is  $\pm \infty$ , that is, it is electrically indifferent. The valence of such an element would then be zero. The table given shows seven series of elements as found in the periodic system, and in heavy type we have the supposed atomic weights of these transition elements of zero valence.

| I. Hydrogen          | 0           |     |     |    | I  |    |     |      | 4   |
|----------------------|-------------|-----|-----|----|----|----|-----|------|-----|
| II. Lithium—Fluorine | 4           | 7   | 9   | 11 | 12 | 14 | 16  | 19   | 20  |
| III. Sodium—Chlorine | 20          | 23  | 24  | 27 | 28 | 31 | 32  | 35.5 | 36  |
| IV. Potassium—Bromin | e <b>30</b> | 39  | 40  | ٠. |    |    | 79  | 80   | 84  |
| V. Rubidium—Iodine   | 84          | 85  | 87  |    |    | ٠. | 125 | 127  | 132 |
| VI. Caesium          | 132         | 133 | 137 |    |    |    |     |      | 212 |
| VII.                 | 212         |     |     |    |    | ٠. |     |      | 292 |

The author goes on to consider the formation of these elements without valence from an hypothetical primal matter. The nature of the periodicity is then to be expressed by means of trigonometric and elliptical functions.

If the atomic weights of the first series of elements from lithium to chlorine be inscribed upon a circle whose periphery is 32, beginning with the atomic weight four, of the first inactive element, the diagram on the following page is gotten.

It is immediately seen that the elements of the first and second quadrant are electro-positive and those of the second and fourth are negative and those have the strongest electrical character which lie nearest to the horizontal diameter. Those nearest to the vertical diameter do not show so definite a character. This behavior brings to mind the function  $\cot x$ , and if we



indicate the atomic weight by a the electrochemical character of all the elements of this group can be expressed thus:  $e = \cot \frac{a-4}{16}\pi.$ 

Of course this formula does not express the absolute value of the chemical character of the elements but only the general course of the dependence of this upon the atomic weights.

Similarly a mathematical expression for the dependence of the valence upon the atomic weights is worked out and found to be

$$v = 4f \left( \sin \frac{a - 4}{16} \pi. \right)^2$$

Similar relations can also be worked out for the other series. The author thinks that this hypothesis of the inactive elements combined with his "New Grouping of the Elements," already mentioned, brings out the periodicity in the properties of the elements as a continuous function; at the same time it enables one to see the reason for the arrangement in groups of two series; and lastly, it considerably lightens the task of the future mathematical treatment of the whole problem.

The mathematical functions of Flavitsky should be compared with those just given.

174. The System of Lecoq de Boisbaudran.—On several occasions this distinguished French chemist has intimated that he was busied with the preparation and perfection of a table of the elements which should present clearly the relationship between them. Much expectation has therefore been aroused and the appearance of the table has been looked forward to with much interest. The discussion relative to the properties of argon and its position among the elements probably induced de Boisbaudran to make an earlier publication than he had intended. At any rate, a paper (263) appeared in March 1895, giving an outline of the chief features of the table but manifestly not in a perfected form.

All will agree with the proposition stated by the author, at the outset, that the classification of the simple substances presents great difficulties and that errors are easily fallen into. Interesting relations are sometimes met with on classifying the elements according to systems which are not merely different but incompatible.

The system upon which he had been engaged for some time is not contradictory to that of Mendeléeff but is from a different point of view. He expressed himself as very well satisfied with its predicting powers.

In presenting a sketch of his system to the public, de Boisbaudran promised to give later a more detailed account. The basis of the system is the selection of certain typical characteristic bodies which he calls the "nodes." The differences between the atomic weights, or as he styles them the "variations," are used in the building up of the table. There are eight families, possessing the same number of elements. The first member of each family is derived from hydrogen. The nodes are placed in one plane and the line of the nodes forms the center of the table.

Setting out from hydrogen, each family is formed by five successive increments, and the conditions are thus as if hydrogen itself resulted from another increment brought to a smaller element. If the node has an atomic weight greater than that of hydrogen by at least 32, then two elements fall between them; if less, then only one. The negative elements occupy the center, the positive the extremities. The elements of even and odd atomicities alternate from the smallest body to the greatest.

The classification is compatible with the hypothesis that the chemical elements are in reality composed of portions of matter much smaller than hydrogen. This is Prout's hypothesis, by extension. Provisionally, as a maximum which he believes too high, he has adopted

the  $\frac{1}{128}$ th part of the hydrogen atomic weight for the unit employed in the calculations. The table, given by de Boisbaudran, is as follows:

|      |               |                    |               | $(?\eta)''$  | $\mathrm{Bi}'$ | Pb"  | T1' |       |
|------|---------------|--------------------|---------------|--------------|----------------|------|-----|-------|
| Ba'' | Cs'           | (?5)"              | I'            | Te"          | Sb'            | Sn"  | In' |       |
| Sr"  | Rb'           | $(?\varepsilon)''$ | Br'           | Se"          | As'            | Ge"  | Ga′ |       |
| Ce"  | $\mathbf{K}'$ | $(?\delta)''$      | C1′           | S''          | $\mathbf{P}'$  | Si'' | A1′ | Nodes |
| Mg'' | Na            | $(?\gamma)''$      | $\mathbf{F}'$ | O''          | N'             | C''  | Bo' |       |
| Ge"  | Li            | $(?\beta)''$       |               |              |                |      |     |       |
| H    | H             | Ĥ                  | H             | $\mathbf{H}$ | H              | H    | H   |       |

He also gave a list of the atomic weights of the first line of elements calculated from hydrogen "using simple empirical relations" which he failed to report. It is impossible, therefore, to form a just idea of his methods or of the value of his table. As to the formation of the elements, he thinks that this must depend upon the introduction of inequalities between the masses of matter, just as forces result from inequalities in the movements of bodies. In each case there is compensation, + 1 and - 1, around an equilibrium which, when once disturbed, is never re-established. "The fiction by which we may represent the formation of the elements by the unequal division of a primitive mass of matter is doubtless imaginary. Inequality must have existed from all eternity in so-called material masses, as well as in motion, by reason of a necessity always present, the cause of which escapes us. But is it not permissible for us to suppose that the material inequalities which represent the elements may be modified as may the vires vivae, though their sum always remains constant?" Hitherto no satisfactory sign of a transformation of the elements,

the one into the other, has been observed; but he remained convinced that such a transformation is realized daily in nature under the influence of forces, or of time, of which we are unable or ignorant how to avail ourselves.

175. Blanshard's Natural Groups and Cross-Analogies. Blanshard notes (223) that the existence of analogies between elements in different groups makes classification difficult. They have to be classed from the point of view of the majority of their properties. The author points out the justice of Ostwald's criticism of Mendeléeff's Typical Elements. These are really links. He discusses the analogies of various elements as B and C, and Cr, Mn and Cl, Al and Be, on one hand, and Al and Cr and Fe, on the other. He thinks that it is the elements occupying corresponding positions in the natural groups, especially in adjoining groups, that show these cross-analogies and speaks of a law of cross-analogies.

176. Solubility as a Clue to the Genesis of the Elements.—In a subsequent paper (261) Blanshard attempts to follow out the clue to the genesis of the elements afforded by the property of solubility. He is apparently led to this by the work of Belohoubek upon the solubilities of the hydrocarbons. Four laws are deduced from rather meagre tables of solubility and certain relations of the atomic weights are pointed out. The only bearing upon the genesis of the elements must lie in the similarity to the compounds of carbon and hydrogen and hence it may be reasoned by analogy that the elements are composite in nature.

177. The Melting Points of the Elements as a Clue to Their Genesis.—Blanshard (225) has endeavored to find in the melting points some clue to the origin and interrelation of the elements. As a starting point he makes use of the fact observed in the series of the fatty acids and in such series of carbon compounds with odd and even numbers of carbon atoms, of the alternate recurrence of high and low melting points with each increment of CH<sub>o</sub>. He deduced the laws: 1. With elements of low atomic weight, the melting point varies directly as the atomic weight. 2. In the higher periodic series of elements the melting points are alternately high and low, with the increase of atomic weight. "That is to say, in all but those which, from their low atomic weight, may reasonably be regarded as the very simplest, a relationship maintains which has been observed in numerous series of organic substances. It is reasonable, therefore, to suppose that such elements with higher atomic weights are in reality substances of a higher grade than others, in that they resemble such highly evolved bodies as carbon compounds, at any rate in respect of melting point."

Blanshard has also considered the atomic heats (224, 226), the specific volumes (227), and boiling points (244), in reference to the Periodic Law and the genesis of the elements. The arguments are deduced from analogies to organic compounds, making the homologous series, etc., of this branch of chemistry a key to the value of the elements.

178. The Position of Argon and Helium in the Periodic System.—A considerable proportion of the papers published upon the periodic system during the year 1895, have borne reference to the position to be assigned the strange new elements discovered by Rayleigh and Ramsay. Some, as Nasini (221), have come to the conclusion that either no faith is to be put in the deductions from the kinetic theory of gases, or the system of Mendeléeff is to be cast aside. Others, as Mendeléeff (236), have expressed their confidence in the system, as being based upon too many natural facts, and confirmed in too many ways, to be overthrown by the discovery of one or two new elements with apparently irreconcilable properties. Others, as Sedgwick (231), Reed (232), &c., have claimed to have anticipated the discovery of argon, at least, by predictions from their systems. Such would seem to be the position taken by de Boisbaudran and Rang (213) also. These will find it difficult to keep their predictions fully in accord with the changes in our knowledge of the properties of these new elements. A far wiser position has been taken by many and that is that it is idle to attempt to fit these or any other supposed elements into a rigid system when their elemental character is yet in question and their properties most imperfectly known.

From the preceding pages of this volume it can be seen that the system is incomplete and imperfect; that it allows abundant room for future discoveries and that these discoveries, with the increased knowledge which they imply, can not fail to modify the system in some measure. At the same time he will feel sure that it is not likely to be overthrown but will stand, in some form, as a great natural truth.

Victor Meyer on the Problems of the Atoms.— Victor Meyer has presented in this lecture (254) the arguments for the unity of matter. The insight given by the periodic system into the connection between the atomic weights and the properties of the elements justifies the assumption that the forms of matter, at present regarded as elements, are really of a composite nature.

Perhaps it will be possible, he thinks, by means of a high temperature (3000°) to separate many apparent elements into their components. Experiments to test this have been undertaken by Meyer. It may be that, by synthetic means, bodies will be prepared similar to the present elements. The author regarded his experiments with iodonium bases, some of which resemble the thallium compounds, as a ground for this hope.

180. Lothar Meyer's Account of the Inception of the Periodic System.—In this brief treatise (250) Lothar Meyer has given the world his last words upon the Periodic Law. One of the papers of Döbereiner is given, and this and the paper of Pettenkofer, claiming priority over Dumas, constitute according to Meyer, the beginning of the Periodic Law. While Pettenkofer undoubtedly gave expression to some of the ideas contained in Dumas' Ipswich address rather more than a year before this address was delivered, it is equally certain that his paper did not follow the train of thought nor contain the brilliant speculations which attracted the attention of the world to the address of Dumas. For

eight years Pettenkofer's work was practically unknown while Dumas' had proved an incentive to a band of earnest workers and was really the cause of Pettenkofer's republication. It may be patriotic in Meyer to give this place among the forerunners of the Periodic Law to Pettenkofer, but it does not belong to him.

Meyer followed up these papers with a brief account of the further development of the system. His desire to prove the justice of the priority claims of Pettenkofer has led him to make some unworthy flings against Dumas.

181. Lea on the Color of the lons and the Atomic Weight Differences.—The elements are divided by the author (253) into three classes; those whose ions are always colorless, those whose ions are always colored, and a smaller (transitional) class whose ions are colored at some valences and colorless at others.

With this division as a basis, the elements can be classified, and Lea has given a table of them, corresponding in a measure with the periodic system. The elements of the third class, he concludes, have nothing in common with the others, cannot be classed with them and probably have a totally different constitution.

Lea devoted some space in his paper to a discussion of the atomic weight differences, giving a systematic table of them, yet failing to bring out any new points.

His table, based upon the color of the ions, placed the classes mentioned above on either side of a straight line, in an ascending series, connecting the two sides by means of the transitional elements.

182. Flavitzky's Function for the Deduction of the Properties.—In 1888 the author (166) gave an expression of the Periodic Law as a function of the cotangent. This has already been referred to and was very similar to the recent work of Thomsen (p. 275) but seems to have escaped his attention.

In a further discussion (256) of the subject, he expresses the dependence of the properties of the elements upon their atomic weights by a formula  $a \cot 2\pi\phi(p)$ , where a is a constant depending upon the choice of the measure of the property and  $\phi(p)$  any function of the atomic weight. Since there is no definite measure of the positive or negative character, a is at present undetermined. Still, for purposes of illustration, the formula is made use of by Flavitzky in certain calculations. Thus it may at least serve for the deduction of the properties qualitatively.

183. Tutton's Comparison of Isomorphous Salts.—It is not possible to do more than refer to this excellent work (259). It points out the line of work which will in the future enable chemists to define more sharply the periodic system and to bring out its full usefulness.

The plan of the research is to take three closely allied elements like potassium, rubidium, and cæsium, and to determine with the utmost accuracy the physical constants of their analogous simple and double salts. This gives a clue to the effect produced by replacing an element by an analogous one in various series of salts.

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